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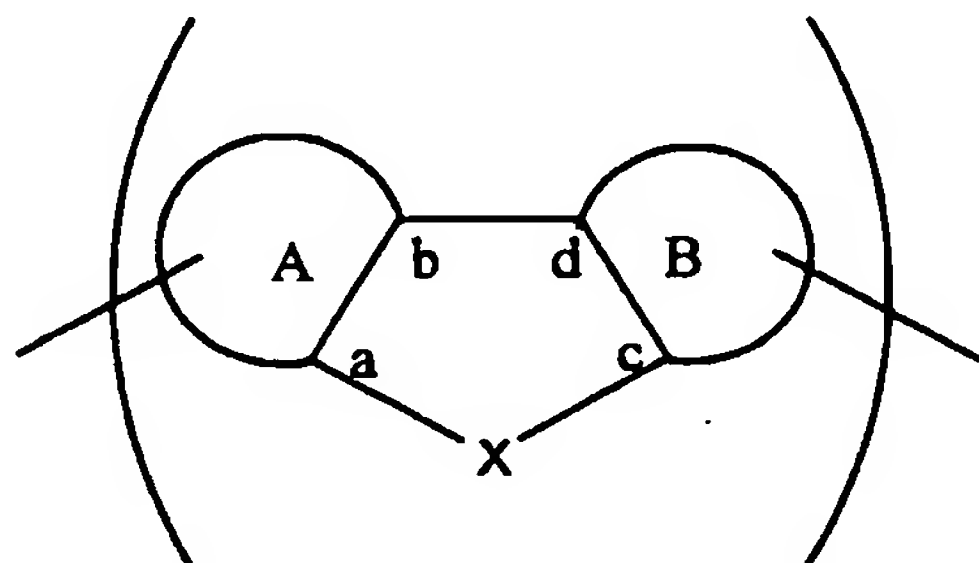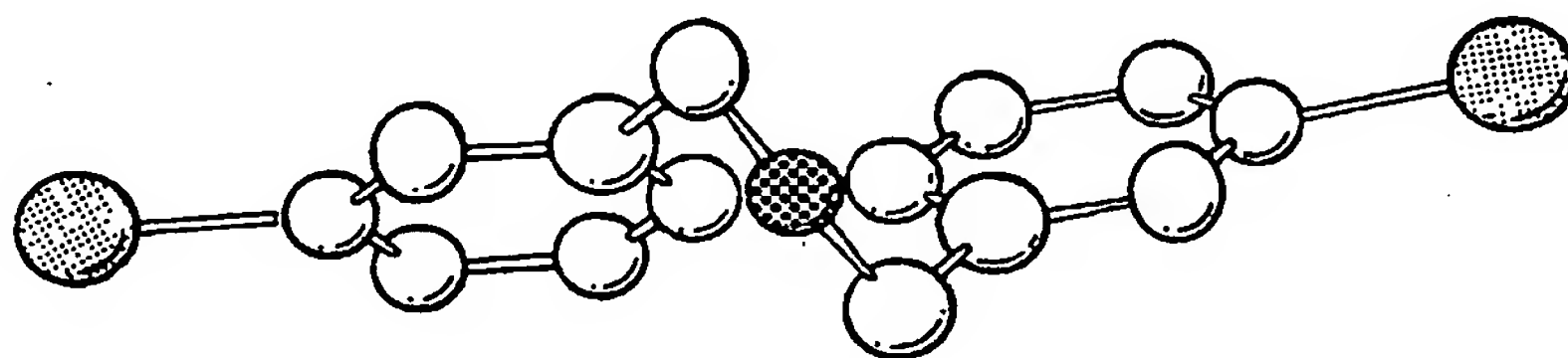
(I)

(57) Abstract: An optical device comprises a substrate and at least one semiconductive polymer supported by said substrate, wherein said semiconductive polymer is a copolymer in which one of the repeat units is a group of formula (I) below or a homopolymer in which the repeat unit is a group of formula (I) below: wherein A and B are the same or different and each comprises wholly or partially an aryl moiety or a heteroaryl moiety, said moiety in A being fused to the bond a-b and said moiety in B being fused to the bond c-d, and X is a linkiing unit, X being such that there is a torsion angle of at least 5° between the bond a-b and the bond c-d about the bond b-d. Semiconductive polymers for use in said devices and monomers for use in the synthesis of said polymers are also provided together with a process fo the synthesis of statistical copolymers.

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TWISTED POLYMERS, USES THEREOF AND PROCESSES FOR THE PREPARATION OF STATISTICAL COPOLYMERS

The present invention relates to optical devices which comprise a substrate which supports at least one semiconductive polymer which is less prone to aggregation than conventional poly(fluorene)-based polymers and which exhibits a blue-shifted emission. It also relates to novel homopolymers and copolymers for use in said devices, monomers for the preparation of said polymers and a process for the preparation of statistical copolymers which is particularly suitable for the preparation of the polymers of the present invention.

In recent years, there has been considerable interest in conjugated polymers. These are polymers which possess a delocalised pi-electron system along the polymer backbone. The delocalised pi-electron system confers semiconducting properties to the polymer and gives it the ability to support positive and negative charge carriers with high mobilities along the polymer chain. Thin films of these conjugated polymers can be used in the preparation of optical devices such as light-emitting devices. These devices have numerous advantages over devices prepared using conventional semiconducting materials, including the possibility of wide area displays, low dc working voltages and simplicity of manufacture. Devices of this type are described in, for example, WO-A-90/13148, US 5,512,654 and WO-A-95/06400.

The world market for displays based on organic and polymeric light-emitting materials has recently been estimated by Stanford Resources, Inc., to be $ 200 million in the year 2002 with a strong growth rate which fuels the high industrial interest in this area (D.E. Mentley, "Flat Information Displays: Market and Technology Trends", 9th edition, 1998). Efficient and highly stable LED devices with low power consumption, which fulfill commercial requirements, have been prepared by a number of companies and academic research groups (see, for example, A. C. Grimsdale et al., *Angew. Chem. Int. Ed.* 1998, *37*, 402; R.H. Friend et al., *Nature* 1999, *397*, 12). As a result of this very fast development of polymer-based LEDs (PLEDs) compared to the development of

inorganic LEDs (Sheats et al., *Science* 1996, *273*, 884) the first effective monochromatic active- and passive-addressed matrix displays have been demonstrated to work and in 1999 PHILIPS announced the initiation of a manufacturing line for PLED display components (e.g. LEP backlights for the automotive and telecommunications industries).

At the moment, great efforts are dedicated to the realization of a full-colour, all plastic screen. The major challenges to achieve this goal are: (1) access to conjugated polymers emitting light of the three basic colours red, green and blue; and (2) the conjugated polymers must be easy to process and fabricate into full-colour display structures. PLED devices show great promise in meeting the first requirement, since manipulation of the emission colour can be achieved by changing the chemical structure of the conjugated polymers. However, while modulation of the chemical nature of conjugated polymers is often easy and inexpensive on the lab scale it can be an expensive and complicated process on the industrial scale. The second requirement of the easy processability and build-up of full-colour matrix devices raises the question of how to micro-pattern fine multicolour pixels and how to achieve full-colour emission. Inkjet printing and hybrid inkjet printing technology have recently attracted much interest for the patterning of PLED devices (see, for example, R.F. Service, *Science* 1998, *279*, 1135; Wudl et al., *Appl. Phys. Lett.* 1998, *73*, 2561; J. Bharathan, Y. Yang, *Appl. Phys. Lett.* 1998, *72*, 2660; and T.R. Hebner, C.C. Wu, D. Marcy, M.L. Lu, J. Sturm, *Appl. Phys. Lett.* 1998, *72*, 519).

In order to contribute to the development of a full-colour display, conjugated polymers exhibiting direct colour-tuning, good processability and the potential for inexpensive large-scale fabrication are sought. The step-ladder polymer poly-2,7-fluorene has been the subject of much research into blue-light emitting polymers (see, for example, A. W. Grice, D. D. C. Bradley, M. T. Bernius, M. Inbasekaran, W. W. Wu, and E. P. Woo, *Appl. Phys. Lett.* 1998, 73, 629; J. S. Kim, R. H. Friend, and F. Cacialli, *Appl. Phys. Lett.* 1999, 74, 3084; WO-A-00/55927 and M. Bernius et al., *Adv. Mater.*, 2000, 12, No. 23, 1737). This class of conjugated polymers possesses excellent processability, endowed by the attachment of solubilizing groups at the remote C-9 position, without

hampering the extended conjugation and therefore leading to high fluorescence quantum
yields in the solid state (up to 79 %) (see, for example, Q. Pei, Y. Yang, *J. Am. Chem.
Soc.* 1996, 118, 7416). Other benefits of poly-2,7-fluorene are its excellent thermal ($T_d >$
400 °C) and chemical stability and its good film forming properties. The rigid nature of
this polymer, however, enhances inter-chain aggregation leading to an undesired red-shift
of the emission colour and a decreasing luminescence efficiency through excimer
formation (see, for example, V. N. Bliznyuk, S. A. Carter, J. C. Scott, G. Klarner, R. D.
Miller, and D. C. Miller, *Macromolecules*, 1999, 32, 361). Aggregation has been
decreased to some extent through statistical copolymerization of 2,7-dibromofluorene
with other halogenated monomers.

The process to make homo- and copolymers based on 9,9-disubstituted fluorene
monomers depends on the metal-mediated cross coupling of both AA-BB and AB type
monomers. There is now a considerable prior art in the field. Such copolymers may be
made by the cross coupling of dibromo-substituted monomers by contacting them with a
Ni(0) catalyst formed *in situ* from a Ni(II) salt (the Yamamoto coupling, *Progress in
Polymer Science*, Vol. 17, p.1153, 1992) (E.P. Woo *et al.*, U.S. 5,708,130; 5,962,631). A
Pd(0) mediated cross coupling between arylboronic acids and esters and aryl or vinyl
halides (the Suzuki coupling, A. Suzuki *et al.*, *Synth. Commun.*, 1981, 11, 513) has been
developed in the presence of a phase transfer catalyst and an inorganic base to make
relatively high quality poly(fluorene) derivatives for applications as PLEDs (M.
Inbasekaran, US 5,777,070). Extension to various comonomers having hole transporting
properties has also been realised (WO-A-99/54385). In a further development a
combination of a catalyst and a base was selected to convert the boron functional groups
into $-BX_3^-$ where X is either F or OH (WO-A-00/53656).

As noted above, it is well known that a major disadvantage of poly(fluorene)-
based homopolymers is their tendency to aggregate in the solid state, resulting in the
formation of excited state complexes (excimers) under conditions of fluorescence through
stimulation by photo-excitation or double charge injection (electroluminescence). One
way of reducing this tendency is to employ copolymers to break up aggregation (see US-

A-5,777,070; D. Kim, et al., *Macromolecules*, 1999, *32*, 1476). Another approach is to use ladder-like planarised polymers (U. Scherf and K. Müllen, *Adv. Polym. Sci.*, 1995, *123*,1) and poly(indenofluorenes (S. Setayesh et al., *Macromolecules*, 2000, *33*, 2016). Dendrimer substituents as end caps (G. Klaerner, R. D. Miller and C. J. Hawker, Abstracts of Papers of the American Chemical Society, 216: 300-POLY, Part 3 Aug, 23 1998) and at the 9-position of the fluorene building block (S. Setayesh et al., *J. Am. Chem. Soc.*, 2001,*123*, 946) have been used to inhibit aggregation. Hole trapping end groups also enhance device performance, possibly through inhibition of aggregate formation.(T. Miteva et al., *Adv. Mater.*, 2001,*13*, 565). It has been noted that poly(1,4-phenylene vinylene) homo- and copolymers carrying a 2,3-disubstitution pattern show a tendency to twist, and this distortion has been used to improve luminescence efficiency of polymer derivatives (see WO-A-01/07052). The origin of the broken conjugation in the backbone *m*-linked polyphenylenes has recently been discussed by S. Y. Hong et al., *Macromolecules*, 2001, *34*, 6474.

It is highly desirable to develop electroluminescent polymers which reduce the aggregation seen in poly(fluorene)-based polymers. In this invention the design of electroluminescent polymers incorporating comonomers based on homologues of fluorene derivatives and optical devices incorporating said polymers is described.

Thus, in a first aspect of the present invention there is provided an optical device which comprises a substrate and at least one semiconductive polymer supported by said substrate, wherein said semiconductive polymer is a copolymer in which one of the repeat units is a group of formula (I) below or a homopolymer in which the repeat unit is a group of formula (I) below:

(I)
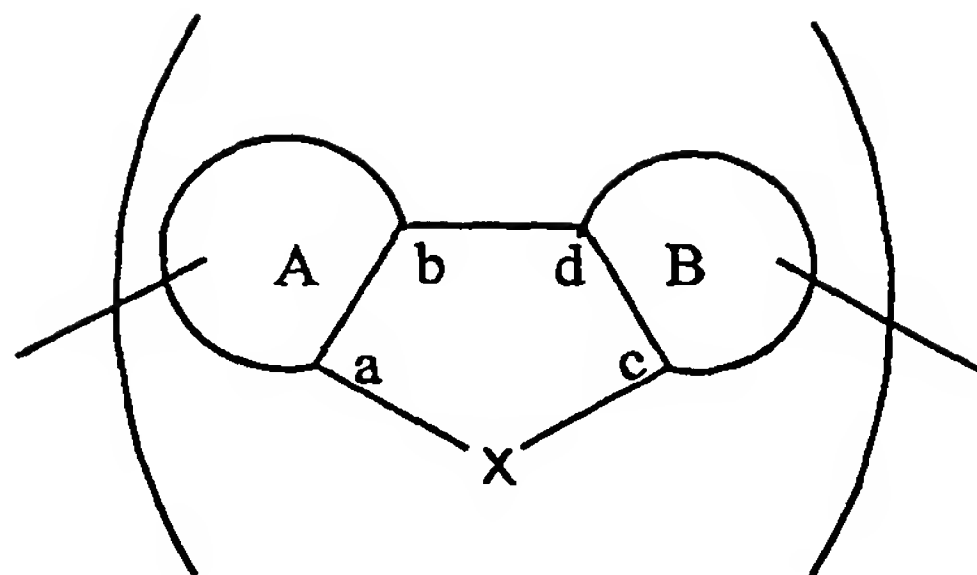
wherein:

A and B are the same or different and each comprises wholly or partially an aryl moiety or a heteroaryl moiety, said moiety in A being fused to the bond a-b and said moiety in B being fused to the bond c-d; and

X is a linking unit, X being such that there is a torsion angle of at least 5° between the bond a-b and the bond c-d about the bond b-d.

The linking unit X is chosen such that A and B are twisted about the bond b-d so that the bonds a-b and c-d are not co-planar but instead there is a torsion angle of at least 5° between the bond a-b and the bond c-d about the bond b-d. Preferably, the torsion angle is from 5° to 75°; more preferably, the torsion angle is from 10° to 70°; yet more preferably, the torsion angle is from 30° to 60°; and most preferably, the torsion angle is from 40° to 55°.

The incorporation of the repeat units of formula (I) above results in the introduction of a degree of twisting to the polymer backbone. This has two effects. First, the overall extent of conjugation in the polymer is reduced which has the effect of increasing the HOMO-LUMO bandgap of these materials leading to a blue-shifted emission. Second, the introduction of twisting in the polymer backbone causes a reduction in the aggregation experienced in existing poly(fluorene)-based polymers.

In the group of formula (I) above, the aryl moiety may be, for example, an aromatic hydrocarbon moeity having from 6 to 14 carbon atoms in one or more rings which may optionally be substituted with at least one substituent, e.g. one or more substituents selected from the group consisting of nitro groups, cyano groups, amino groups, alkyl groups as defined below, haloalkyl groups as defined below, alkoxyalkyl groups as defined below, aryloxy groups as defined below and alkoxy groups as defined below. Examples of the aryl moieties include phenyl, naphthyl, phenanthryl and anthracenyl groups.

In the group of formula (I) above, the heteroaryl moiety may be, for example, a 5- to 7-membered aromatic heterocyclic moiety containing from 1 to 3 heteroatoms selected from the group consisting of sulfur atoms, oxygen atoms and nitrogen atoms, said moiety optionally being substituted with at least one substituent, e.g. one or more substituents selected from the group consisting of nitro groups, cyano groups, amino groups, alkyl groups as defined below, haloalkyl groups as defined below, alkoxyalkyl groups as defined below, aryloxy groups as defined below and alkoxy groups as defined below. Examples of such heteroaryl groups include furyl, thienyl, pyrrolyl, pyrazolyl, imidazolyl, oxazolyl, isoxazolyl, thiazolyl, isothiazolyl, triazolyl, tetrazolyl, thiadiazolyl, pyridyl, pyridazinyl, pyrimidinyl and pyrazinyl groups.

The alkyl groups above are straight or branched-chain alkyl groups having from 1 to 20 carbon atoms.

The haloalkyl groups above are alkyl groups as defined above which are substituted with at least one halogen atom.

The alkoxy groups above are straight or branched-chain alkoxy groups having from 1 to 20 carbon atoms.

The alkoxyalkyl groups above are alkyl groups as defined above which are substituted with at least one alkoxy group as defined above.

The aryl moiety of the aryloxy groups above is an aromatic hydrocarbon group having from 6 to 14 carbon atoms in one or more rings which may optionally be substituted with at least one substituent selected from the group consisting of nitro

groups, cyano groups, amino groups, alkyl groups as defined above, haloalkyl groups as defined above, alkoxyalkyl groups as defined above and alkoxy groups as defined above.

Preferably, there is provided an optical device which comprises a substrate and at least one semiconductive polymer supported by said substrate, wherein said semiconductive polymer is a copolymer in which one of the repeat units is a group of formula (II) below or a homopolymer in which the repeat unit is a group of formula (II) below:
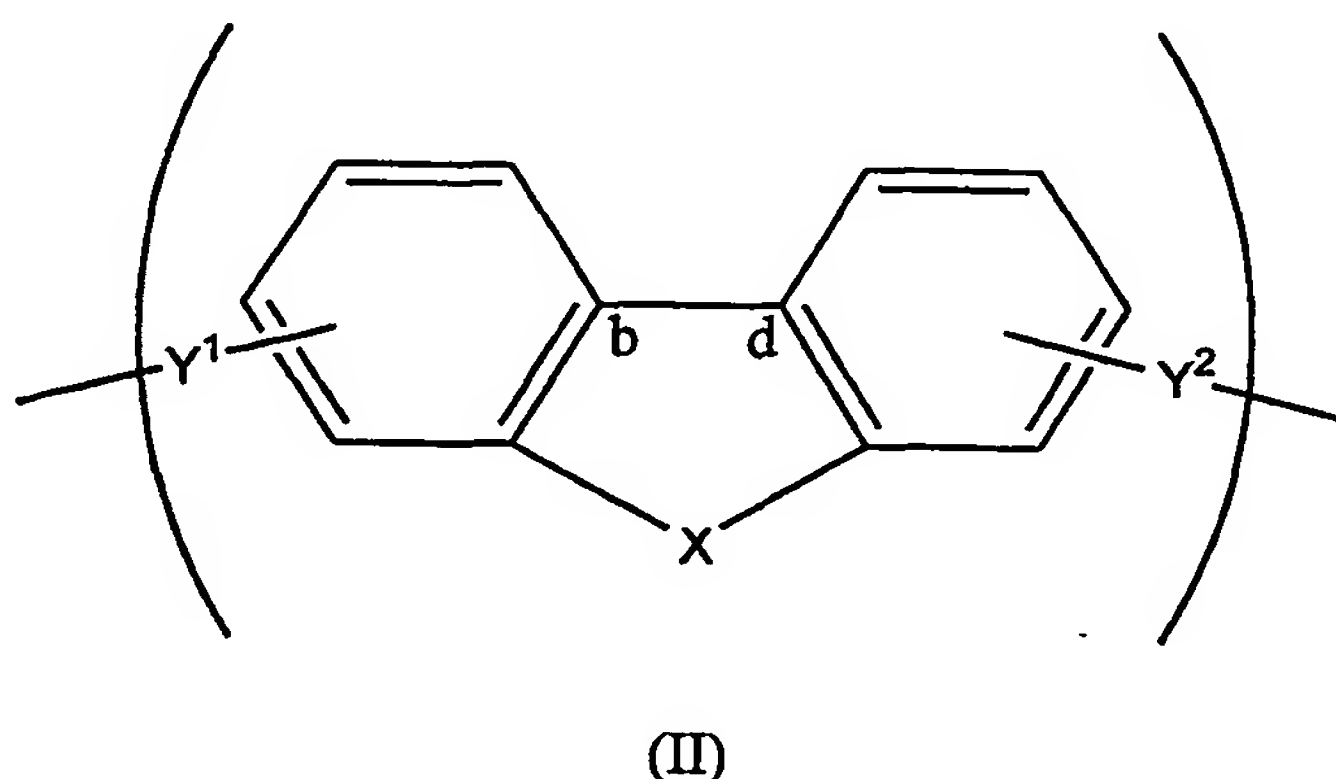
(II)

wherein:

Y^1 and Y^2 are the same or different and each represents a single bond or a linking unit that is conjugated with the phenyl group to which it is attached; and

X is a linking unit, X being such that there is a torsion angle of at least 5° between the two phenyl groups about the bond b-d.

Where Y^1 or Y^2 is a linking unit that is conjugated with the phenyl group to which it is attached, the linking unit and the phenyl group to which it is attached together form a conjugated moiety which links the unit of formula (II) to the next unit in the copolymer or homopolymer. Thus, for example, Y^1 can be a phenyl group which is fused with the phenyl group to which it is attached to give a naphthylene linking unit, or an indenyl group which is fused with the phenyl group to which it is attached to give a fluorenyl linking unit.

More preferably, there is provided an optical device which comprises a substrate and at least one semiconductive polymer supported by said substrate, wherein said semiconductive polymer is a copolymer in which one of the repeat units is a group of formula (III) below or a homopolymer in which the repeat unit is a group of formula (III) below:

(III)

wherein:

m and n are the same or different and each is 0 or an integer of 1, 2 or 3;

R^1 and R^2 are same or different and each is selected from the group consisting of alkyl groups as defined above, haloalkyl groups as defined above, alkoxy groups as defined above, alkoxyalkyl groups as defined above, aryl groups (comprising aromatic hydrocarbon groups having from 6 to 14 carbon atoms in one or more rings which may optionally be substituted with at least one substituent selected from the group consisting of nitro groups, cyano groups, amino groups, alkyl groups as defined above, haloalkyl groups as defined above, alkoxyalkyl groups as defined above and alkoxy groups as defined above), aryloxy groups as defined above, and aralkyl groups comprising an alkyl group as defined above which is substituted with at least one aryl group as defined above; and

X is a linking unit, X being such that there is a torsion angle of at least 5° between the two phenyl rings about the bond b-d. Where there is more than one group R^1 and/or R^2, then each R^1 or R^2 may be the same or different from the others.

In the optical devices of the present invention where the repeat unit in the copolymer or homopolymer is a group of formula (III), X is preferably a moiety of formula -A-B-C- wherein A, B and C are the same or different and each is selected from the group consisting of O, S, SO, SO_2, NR^3, $N^+(R^{3'})(R^{3''})$, $C(R^4)(R^5)$, $Si(R^{4'})(R^{5'})$, and $P(O)(OR^6)$, wherein:

R^3, $R^{3'}$ and $R^{3''}$ are the same or different and each is selected from the group consisting of hydrogen atoms, alkyl groups as defined above, haloalkyl groups as defined above, alkoxy groups as defined above, alkoxyalkyl groups as defined above, aryl groups as defined above, aryloxy groups as defined above, aralkyl groups as defined above, and alkyl groups as defined above which are substituted with at least one group of formula $-N^+(R^7)_3$ wherein each group R^7 is the same or different and is selected from the group consisting of hydrogen atoms, alkyl groups as defined above and aryl groups as defined above;

R^4, R^5, $R^{4'}$ and $R^{5'}$ are the same or different and each is selected from the group consisting of hydrogen atoms, alkyl groups as defined above, haloalkyl groups as defined above, alkoxy groups as defined above, halogen atoms, nitro groups, cyano groups, alkoxyalkyl groups as defined above, aryl groups as defined above, aryloxy groups as defined above, aralkyl groups as defined above and alkyl groups as defined above which are substituted with a substituent selected from the group consisting of aryl groups as defined above, heteroaryl groups as defined below, fluorenyl groups and spirobifluorenyl groups, said aryl, heteroaryl, fluorenyl and spirobifluorenyl groups being substituted with a disubstituted amino group the substituents of which are the same or different and are selected from the group consisting of aryl groups as defined above, heteroaryl groups as defined below, fluorenyl groups and spirobifluorenyl groups, or R^4 and R^5 together with the carbon atom to which they are attached represent a carbonyl group; and

R^6 is selected from the group consisting of hydrogen atoms, alkyl groups as defined above, haloalkyl groups as defined above, alkoxyalkyl groups as defined above, aryl groups as defined above, aryloxy groups as defined above and aralkyl groups as defined above;

said heteroaryl groups are 5- to 7-membered aromatic heterocyclic groups containing from 1 to 3 heteroatoms selected from the group consisting of sulfur atoms,

oxygen atoms and nitrogen atoms, said groups optionally being substituted with at least one substituent selected from the group consisting of nitro groups, cyano groups, amino groups, alkyl groups as defined above, haloalkyl groups as defined above, alkoxyalkyl groups as defined above, aryloxy groups as defined above and alkoxy groups as defined above.

Preferably, R^3, $R^{3'}$ and $R^{3''}$ are the same or different and each is selected from the group consisting of hydrogen atoms and alkyl groups having from 1 to 6 carbon atoms which are optionally substituted with a group of formula $-N^+(R^7)_3$ wherein each group R^7 is the same or different and is selected from the group consisting of hydrogen atoms and alkyl groups having from 1 to 6 carbon atoms; more preferably, R^3, $R^{3'}$ and $R^{3''}$ are the same or different and each represents an alkyl group having from 1 to 3 carbon atoms which is optionally substituted with a group of formula $-N^+(R^7)_3$ wherein each group R^7 is the same or different and is an alkyl group having from 1 to 3 carbon atoms.

Preferably, R^4, R^5, $R^{4'}$ and $R^{5'}$ are the same or different and each is selected from the group consisting of hydrogen atoms, alkyl groups having from 1 to 10 carbon atoms, alkoxy groups having from 1 to 10 carbon atoms and alkyl groups having from 1 to 10 carbon atoms (e.g. methyl groups) which are substituted with a substituent selected from the group consisting of aryl groups, heteroaryl groups, fluorenyl groups and spirobifluorenyl groups, said aryl, heteroaryl, fluorenyl and spirobifluorenyl groups being substituted (preferably at a position para to the alkyl group) with a disubstituted amino group the substituents of which are the same or different and are selected from the group consisting of aryl groups, heteroaryl groups, fluorenyl groups and spirobifluorenyl groups; more preferably, R^4, R^5, $R^{4'}$ and $R^{5'}$ are the same or different and each is selected from the group consisting of hydrogen atoms, alkyl groups having from 1 to 3 carbon atoms and alkoxy groups having from 5 to 10 carbon atoms; and most preferably, each of R^4, R^5 or $R^{4'}$ and $R^{5'}$ is a hydrogen atom or R^4 or $R^{4'}$ represents a hydrogen atom and R^5 or $R^{5'}$ represents an alkoxy group having from 7 to 10 carbon atoms.

Preferably, R^6 represents a hydrogen atom or an alkyl group having from 1 to 6 carbon atoms; and most preferably a hydrogen atom or an alkyl group having from 1 to 3 carbon atoms.

Preferred examples of the repeat unit of formula (III) are those wherein m and n are each 0 and X is a linking unit of formula -A-B-C- wherein:

(i)   A and C each represent a methylene group and B is selected from the group consisting of O, S, SO_2, NR^3, $N^+(R^{3'})(R^{3''})$ and $C(R^4)(R^5)$ wherein R^3, $R^{3'}$, $R^{3''}$, R^4, R^5 and R^6 are as defined in the above definition of the repeat unit of formula (III);

(ii)   A and C each represent a methylene group and B is selected from the group consisting of O, S, SO_2, NR^3 wherein R^3 is selected from the group consisting of hydrogen atoms and alkyl groups having from 1 to 6 carbon atoms which are optionally substituted with a group of formula $-N^+(R^7)_3$ wherein each group R^7 is the same or different and is selected from the group consisting of hydrogen atoms and alkyl groups having from 1 to 6 carbon atoms, $N^+(R^{3'})(R^{3''})$ wherein $R^{3'}$ and $R^{3''}$ are the same or different and each represents an alkyl group having from 1 to 6 carbon atoms which is optionally substituted with a group of formula $-N^+(R^7)_3$ wherein each group R^7 is the same or different and is selected from the group consisting of hydrogen atoms and alkyl groups having from 1 to 6 carbon atoms, and $C(R^4)(R^5)$ wherein R^4 and R^5 are the same or different and each is selected from the group consisting of hydrogen atoms, alkyl groups having from 1 to 10 carbon atoms, alkoxy groups having from 1 to 10 carbon atoms and alkyl groups having from 1 to 10 carbon atoms (e.g. methyl groups) which are substituted with a substituent selected from the group consisting of aryl groups, heteroaryl groups, fluorenyl groups and spirobifluorenyl groups, said aryl, heteroaryl, fluorenyl and spirobifluorenyl groups being substituted (preferably at a position para to the alkyl group) with a disubstituted amino group the substituents of which are the same or different and are selected from the group consisting of aryl groups, heteroaryl groups, fluorenyl groups and spirobifluorenyl groups;

(iii)   A and C each represent a methylene group and B is selected from the group consisting of O, S, SO_2, $N^+(R^{3'})(R^{3''})$ wherein $R^{3'}$ and $R^{3''}$ are the same or different and each represents an alkyl group having from 1 to 3 carbon atoms which is optionally

substituted with a group of formula $-N^+(R^7)_3$ wherein each group R^7 is the same or different and is an alkyl group having from 1 to 3 carbon atoms, and $C(R^4)(R^5)$ wherein R^4 and R^5 are the same or different and each is selected from the group consisting of hydrogen atoms, alkyl groups having from 1 to 3 carbon atoms and alkoxy groups having from 5 to 10 carbon atoms, particularly wherein each of R^4 and R^5 is a hydrogen atom or R^4 represents a hydrogen atom and R^5 represents an alkoxy group having from 7 to 10 carbon atoms;

(iv)   A and C each represent O or S and B is selected from the group consisting of O, S, SO_2, NR^3, $N^+(R^{3'})(R^{3''})$ and $C(R^4)(R^5)$ wherein R^3, $R^{3'}$, $R^{3''}$, R^4, R^5 and R^6 are as defined in the above definition of the repeat unit of formula (III);

(v)   A and C each represent O or S and B is a group of formula $C(R^4)(R^5)$ wherein R^4 and R^5 are the same or different and each represents a hydrogen atom or an alkyl group having from 1 to 10 carbon atoms; or

(vi)   A and C each represent O and B is a group of formula $C(R^4)(R^5)$ wherein R^4 and R^5 are the same or different and each represents an alkyl group having from 1 to 3 carbon atoms.
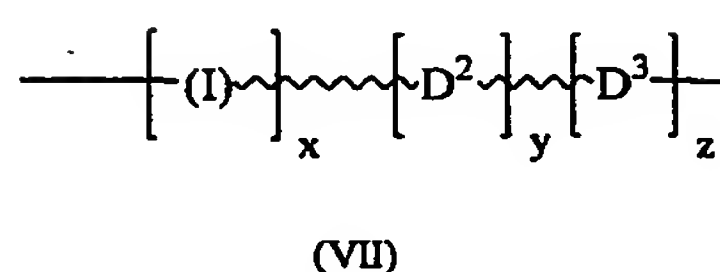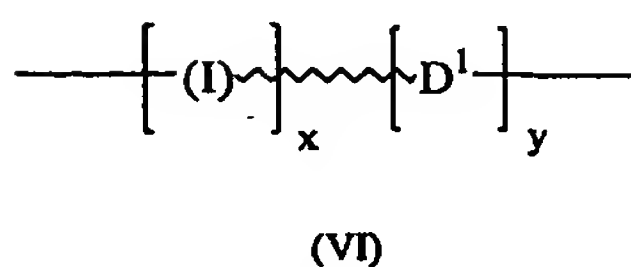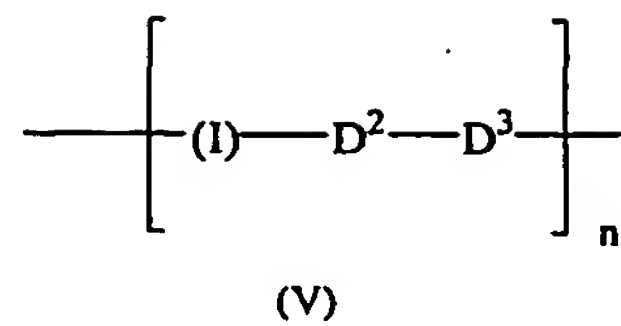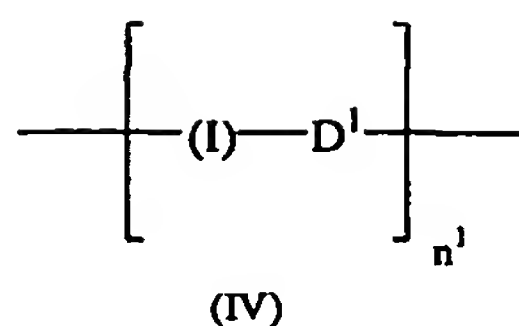
Particularly preferred repeat units are selected from the following group:
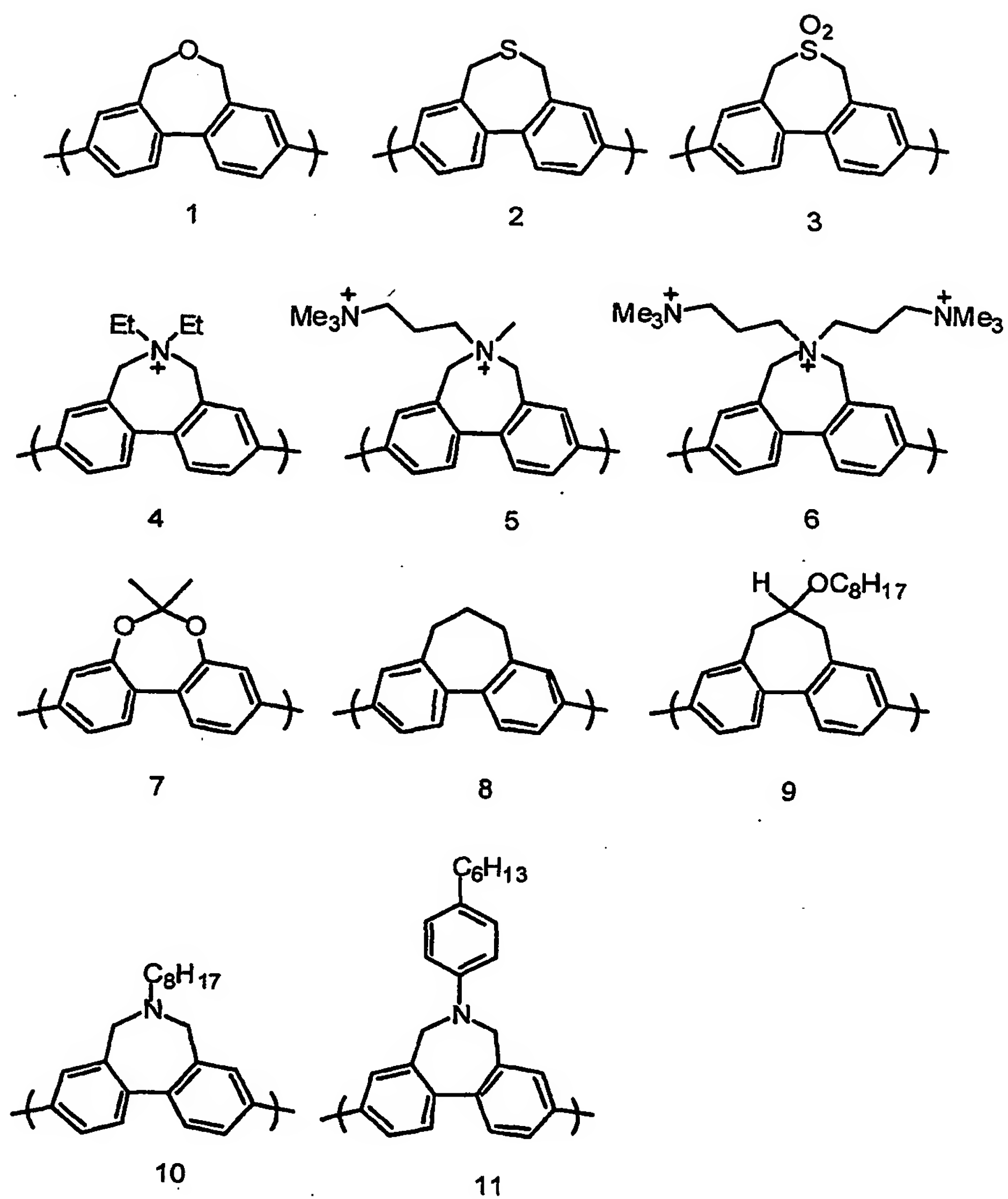
Selection of Repeat Units 1-11

Many of the semiconductive polymers used in the optical devices of the present invention are novel. Therefore, in a further aspect of the present invention, there is provided a semiconductive copolymer in which one of the repeat units is a group of formula (II) as defined above or a semiconductive homopolymer in which the repeat unit is a group of formula (II) as defined above, with the proviso that, where Y^1 and Y^2 each represent a single bond, X may not represent a linking unit selected from the group consisting of $-CO-O-CO-$, $-CO-NH-CO-$ and $-O-P(O)(OH)-O-$, and where Y^1 represents a phenyl group which is fused with the phenyl group to which it is attached to form a naphthalenyl group and Y^2 represents a phenyl group which is fused with the phenyl group to which it is attached to form a naphthalenyl group, X may not represent a group of formula $-O-CH_2-O-$.

Preferably, the semiconductive polymer of the present invention is a copolymer in which one of the repeat units is a group of formula (III) as defined above or a homopolymer in which the repeat unit is a group of formula (III) as defined above, with the proviso that, where Y^1 and Y^2 each represent a single bond, X may not represent a linking unit selected from the group consisting of $-CO-O-CO-$, $-CO-NH-CO-$ and $-O-P(O)(OH)-O-$. The preferred, more preferred and most preferred options for substituents R^3, $R^{3'}$, $R^{3''}$, R^4, R^5, R^6 and R^7 and the linking unit $-A-B-C-$ in the repeat unit of formula (III) of the copolymers and homolpolymers of the invention are as recited above for the optical devices of the present invention.

Preferably, the polymers used in the optical devices of the present inventions are copolymers or terpolymers. These copolymers include alternating AB copolymers and terpolymers, and statistical copolymers and terpolymers. These can be depicted by the following general formulae (IV), (V), (VI) and (VII):

$$-\left[(I)\!-\!D^1 \right]_{n^1}$$
$$\text{(IV)}$$

$$-\left[(I)\!-\!D^2\!-\!D^3 \right]_{n^1}$$
$$\text{(V)}$$

$$-\left[(I) \right]_x \!\!\sim\!\! \left[D^1 \right]_y -$$
$$\text{(VI)}$$

$$-\left[(I) \right]_x \!\!\sim\!\! \left[D^2 \right]_y \!\!\sim\!\! \left[D^3 \right]_z -$$
$$\text{(VII)}$$

wherein:

(I) is a repeat unit as defined above, D^1, D^2 and D^3 are repeat units which are conjugated with the adjacent units in the polymer chain, n^1 is an integer greater than 3, the ratio of x:y is from 99:1 to 1:99, and the ratio of x:(y+z) is from 99:1 to 1:99.

The repeat units D^1, D^2 and D^3 are any conjugated units commonly used in electroluminescent polymers, e.g. those disclosed in Burroughes et al., Nature, 1990, **347**, 539; WO-A-93/14177; WO-A-94/29883; US-A-5,514,878; WO-A-99/54385; US-A-5,672,678; WO-A-00/55927; EP-A-0707020; and co-pending application PCT/GB00/04594. Specific examples include the following conjugated units of formulae (VIII), (IX), (X), (XI), (XII), (XIII), (XIV) and (XV):
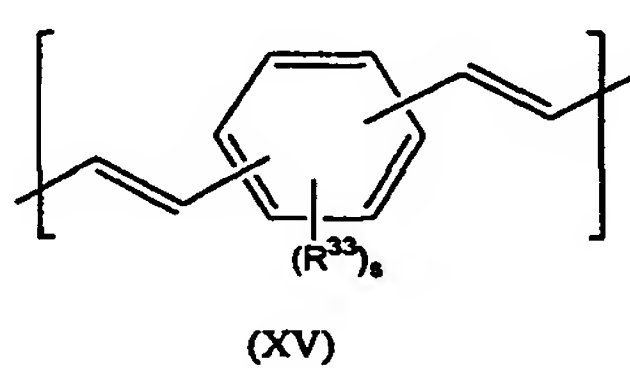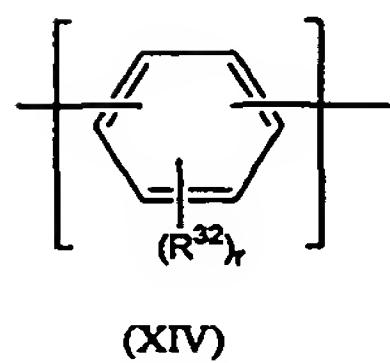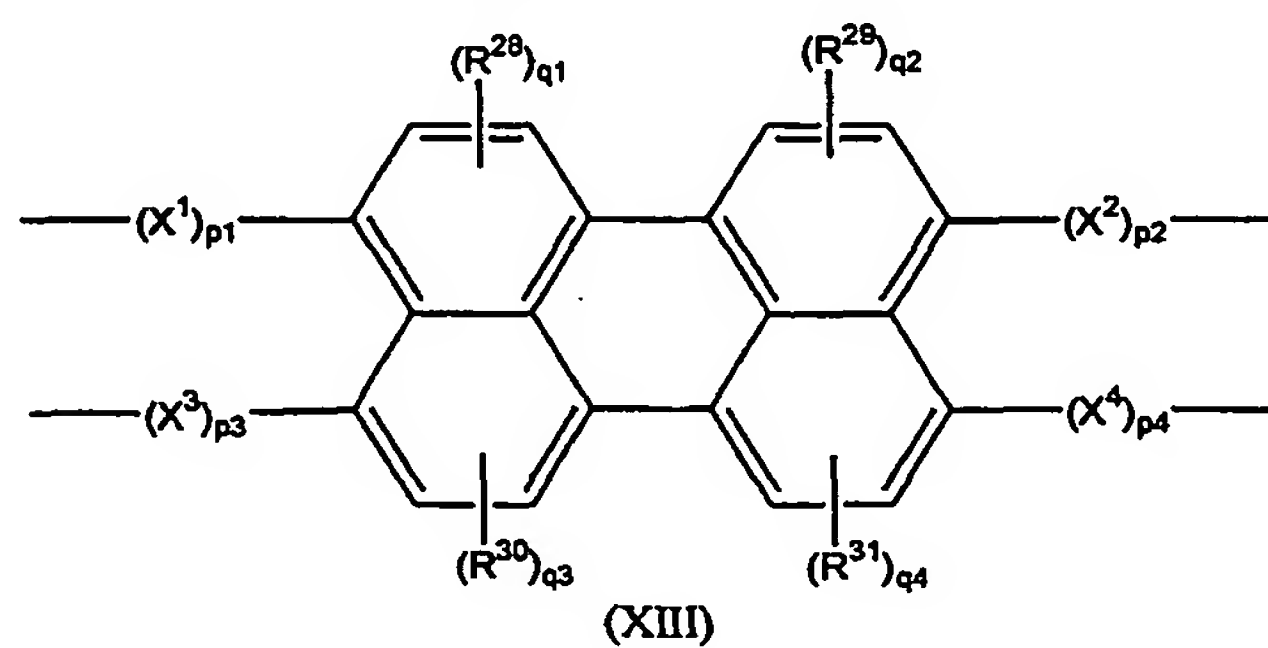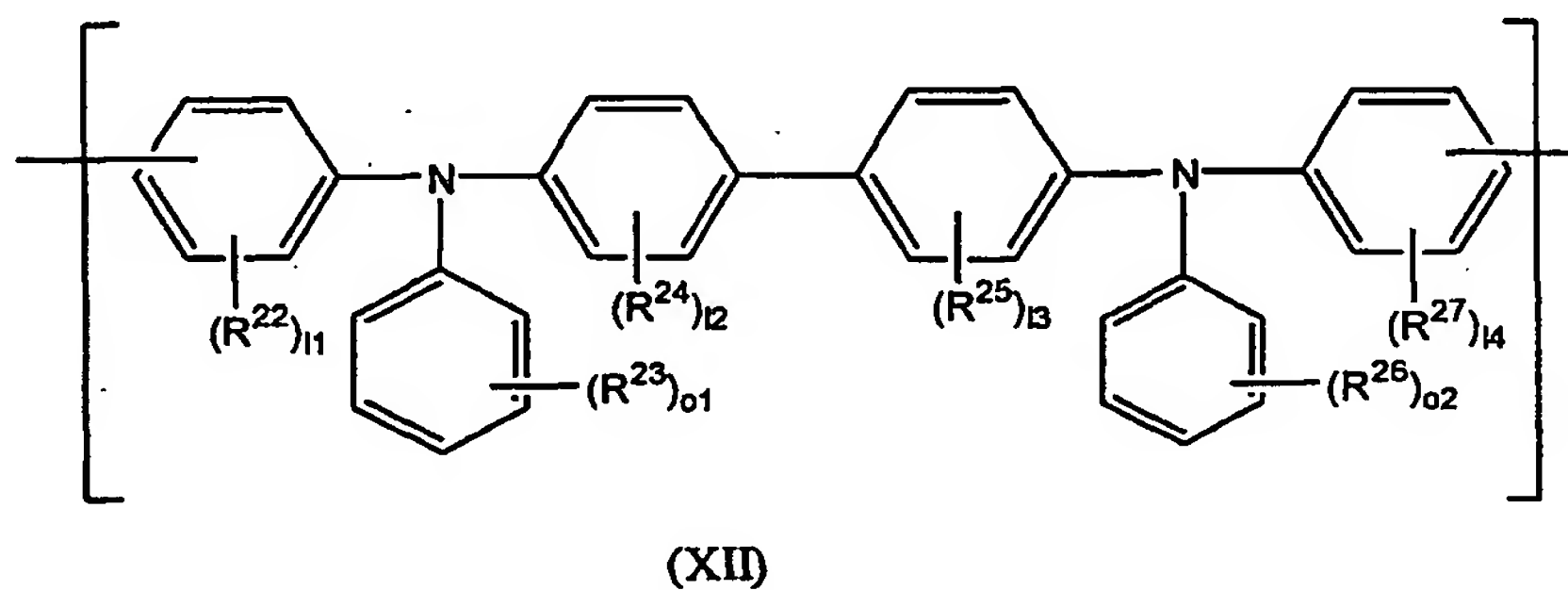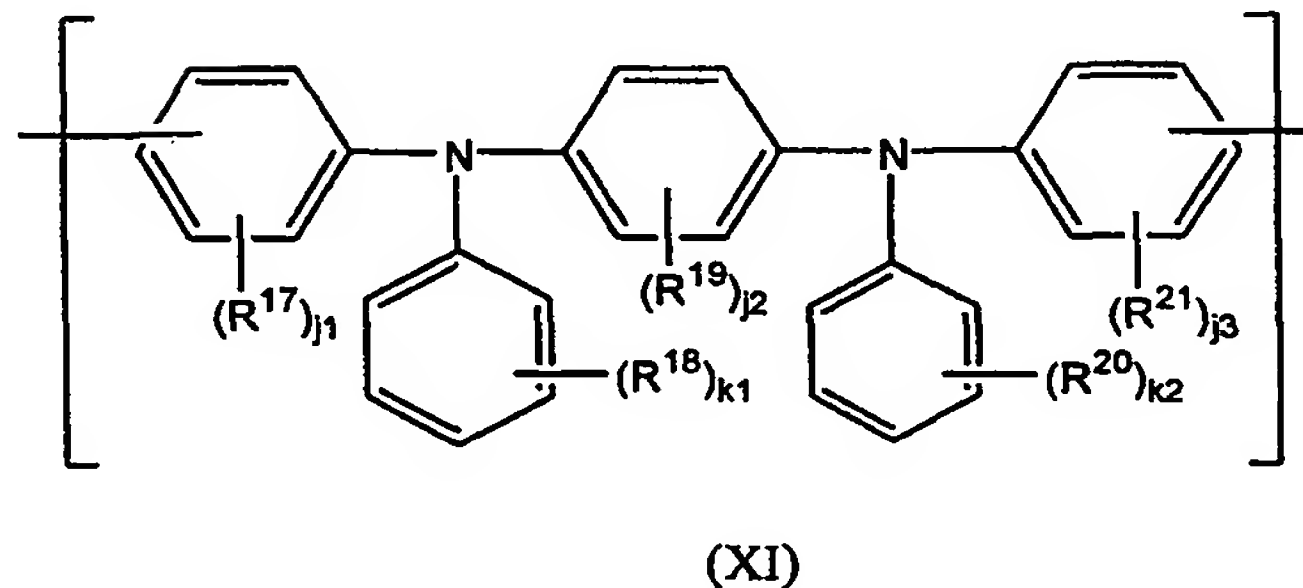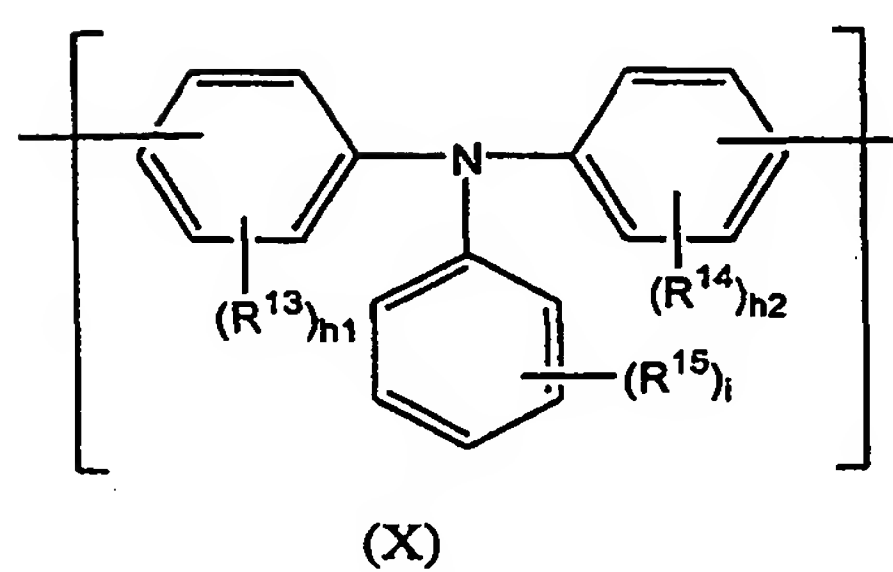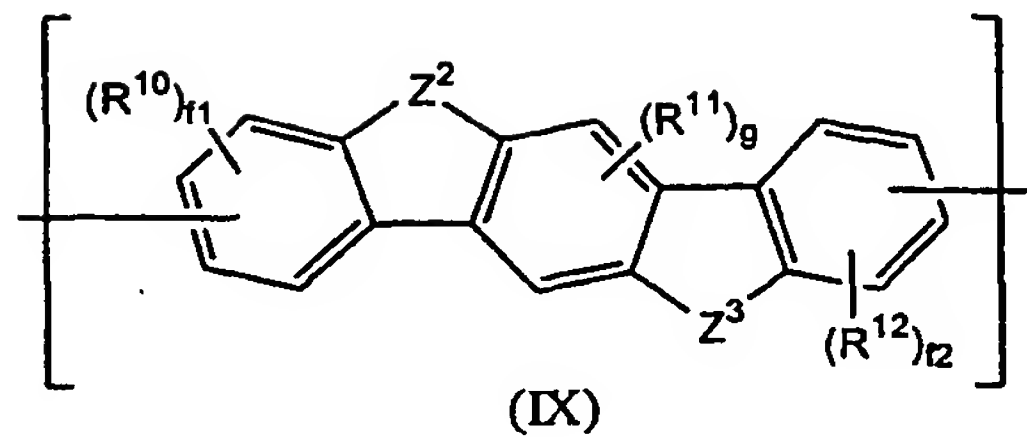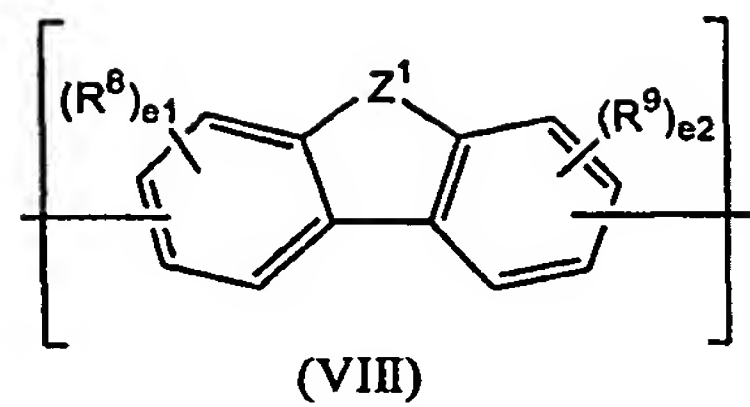
(VIII)

(IX)

(X)

(XI)

(XII)

(XIII)

(XIV)

(XV)

wherein:

each of R^8 to R^{15} and R^{17} to R^{33} is the same or different and is selected from the group consisting of alkyl groups as defined above, haloalkyl groups as defined above, alkoxy groups as defined above, alkoxyalkyl groups as defined above, aryl groups as defined above, aryloxy groups as defined above, aralkyl groups as defined above and groups of formula $-COR^{16}$ wherein R^{16} is selected from the group consisting of hydroxy groups, alkyl groups as defined above, haloalkyl groups as defined above, alkoxy groups as defined above, alkoxyalkyl groups as defined above, aryl groups as defined above, aryloxy groups as defined above, aralkyl groups as defined above, amino groups, alkylamino groups the alkyl moiety of which is as defined above, dialkylamino groups wherein each alkyl moiety is the same or different and is as defined above, aralkyloxy groups the aralkyl moiety of which is as defined above and haloalkoxy groups comprising an alkoxy group as defined above which is substituted with at least one halogen atom;

each of Z^1, Z^2 and Z^3 is the same or different and is selected from the group consisting of O, S, SO, SO_2, NR^3, $N^+(R^{3'})(R^{3''})$, $C(R^4)(R^5)$, $Si(R^{4'})(R^{5'})$ and $P(O)(OR^6)$, wherein R^3, $R^{3'}$, $R^{3''}$, R^4, R^5, $R^{4'}$, $R^{5'}$ and R^6 are as defined above;

each of X^1, X^2, X^3 and X^4 is the same or different and is selected from:
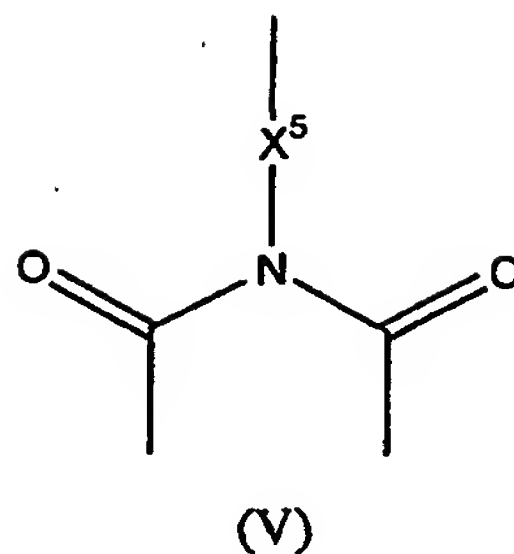
    aryl moieties as defined above;

    straight or branched-chain alkylene groups having from 1 to 6 carbon atoms;

    straight or branched-chain alkenylene groups having from 2 to 6 carbon atoms; and

    straight or branched-chain alkynylene groups having from 1 to 6 carbon atoms; or

    X^1 and X^2 together and/or X^3 and X^4 together can represent a linking group of formula (V) below:

(V)

wherein X^5 represents an aryl moiety as defined above;

each of e1, e2, f1 and f2 is the same or different and is 0 or an integer of 1 to 3;

each of g, q1, q2, q3 and q4 is the same or different and is 0, 1 or 2;

each of h1, h2, j1, j2, j3, l1, l2, l3, l4, r and s is the same or different and is 0 or an integer of 1 to 4;

each of i, k1, k2, o1 and o2 is the same or different and is 0 or an integer of 1 to 5; and

each of p1, p2, p3 and p4 is 0 or 1.

In the above alternating AB copolymers and terpolymers, and statistical copolymers and terpolymers of general formulae (IV), (V), (VI) and (VII), the following are preferred:

(A)   those wherein the repeat unit (I) is a repeat unit of formula (II) as defined above;

(B)   those wherein the repeat unit (I) is a repeat unit of formula (III) as defined above;

(C)   those wherein the repeat unit (I) is one of the preferred, more preferred and most preferred units of formula (III) described above;

(D)   those wherein the repeat units D^1, D^2 and D^3 are selected from the group consisting of units of formulae (VIII), (IX), (XIV) and (XV) as defined above;

(E)   those wherein the repeat unit D^1, D^2 or D^3 is a unit of formula (VIII) wherein Z^1, Z^2 and Z^3 are selected from the group consisting of O, S and $C(R^4)(R^5)$ wherein R^4 and R^5 are as defined above;

(F)   those wherein the repeat unit D^1, D^2 or D^3 is a unit of formula (VIII) wherein each of e1 and e2 is 0 and Z^1, Z^2 or Z^3 is a group of formula $C(R^4)(R^5)$ wherein R^4 and R^5 are the same or different and are selected from the group consisting of hydrogen atoms, alkyl groups having from 1 to 10 carbon atoms (e.g. n-hexyl, n-octyl, 2-ethylhexyl and 3,7-dimethyloctyl groups) and alkyl groups having from 1 to 10 carbon atoms (e.g. methyl groups) which are substituted with a substituent selected from the group consisting of aryl groups, heteroaryl groups, fluorenyl groups and spirobifluorenyl groups, said aryl, heteroaryl, fluorenyl and spirobifluorenyl groups being substituted (preferably at the para position) with a disubstituted amino group the substituents of which are the same or different and are selected from the group consisting of aryl groups, heteroaryl groups, fluorenyl groups and spirobifluorenyl groups;

(G)   those wherein the repeat unit D^1, D^2 or D^3 is a unit of formula (XV) having the following formula:
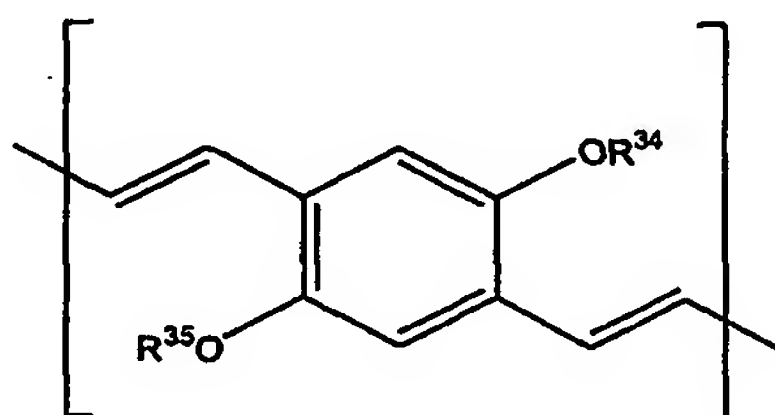
wherein R^{34} and R^{35} are the same or different and each is an alkyl group as defined above;

(H)   statistical copolymers of formula (VI) wherein the ratio x:y is from 10:90 to 50:50;

(I)   statistical copolymers of formula (VI) wherein the ratio x:y is from 10:90 to 45:55.

Of these, preferred are those alternating AB copolymers and terpolymers, and statistical copolymers and terpolymers of general formulae (IV), (V), (VI) and (VII)

wherein the repeat unit (I) is as defined in (A) and the repeat units D^1, D^2 and D^3 are as defined in (D); more preferred are those alternating AB copolymers and terpolymers, and statistical copolymers and terpolymers of general formulae (IV), (V), (VI) and (VII) wherein the repeat unit (I) is as defined in (B) and the repeat units D^1, D^2 and D^3 are as defined in (E) or (G); yet more preferred are those alternating AB copolymers and terpolymers, and statistical copolymers and terpolymers of general formulae (IV), (V), (VI) and (VII) wherein the repeat unit (I) is as defined in (C) and the repeat units D^1, D^2 and D^3 are as defined in (E) or (G); particularly preferred are those alternating AB copolymers and terpolymers, and statistical copolymers and terpolymers of general formulae (IV), (V), (VI) and (VII) wherein the repeat unit (I) is as defined in (C) and the repeat units D^1, D^2 and D^3 are as defined in (F) or (G); and most preferred are the statistical copolymers of formula (VI) as defined in (H) wherein the repeat unit (I) is as defined in (C) and the repeat unit D^1 is as defined in (F) or (G).
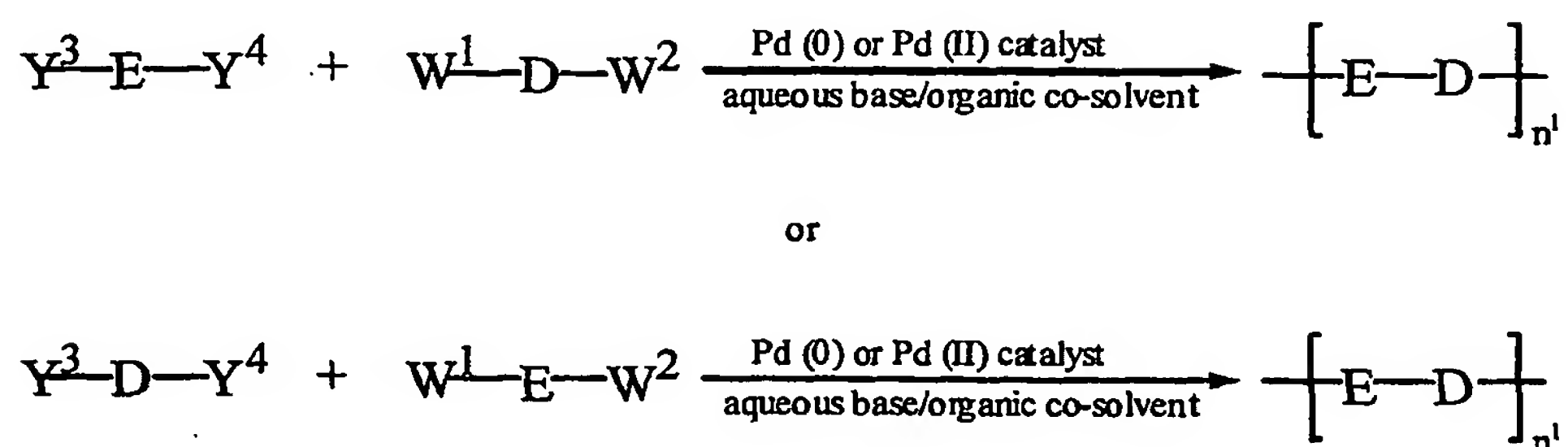
The optical devices of the present invention may comprise a semiconductive polymer of the present invention alone supported by a substrate or the semiconductive polymer of the present invention may be blended with further semiconductive polymers, for example as disclosed in WO-A-99/48160.

The semiconductive polymers used in the preparation of the optical devices of the present invention can be prepared using any of the polymerisations provided by the standard families of polycondensation techniques (e.g. Heck, Suzuki, Yamamoto, Horner, Wessling and Gilch polycondensation techniques; see US-A-5,777,070 and the review article "Electroluminescent Conjugated Polymers - Seeing Polymers in a New Light", A. Kraft, A.C. Grimsdale and A.B. Holmes, *Angew. Chem. Int. Ed. Engl.*, 1998, 37, 402-428, the contents of which are incorporated herein by reference thereto). The choice of the desired monomers and the suitable polycondensation techniques can be made by the person skilled in this field depending upon the nature of the target semiconductive polymer of the present invention.

One of the preferred techniques due to its simplicity and flexibility is the Suzuki

reaction. Thus, the polymers of the present invention may be synthesised according to the Scheme 1 below:

Scheme 1

$$Y^3\text{—}E\text{—}Y^4 \ + \ W^1\text{—}D\text{—}W^2 \xrightarrow[\text{aqueous base/organic co-solvent}]{\text{Pd (0) or Pd (II) catalyst}} \left[\!\!\begin{array}{c} E\text{—}D \end{array}\!\!\right]_{n^1}$$

or

$$Y^3\text{—}D\text{—}Y^4 \ + \ W^1\text{—}E\text{—}W^2 \xrightarrow[\text{aqueous base/organic co-solvent}]{\text{Pd (0) or Pd (II) catalyst}} \left[\!\!\begin{array}{c} E\text{—}D \end{array}\!\!\right]_{n^1}$$

wherein:

E is a repeat unit of formula (I), (II) or (III) as defined above;

D is a repeat unit of formula D^1, D^2 or D^3 as defined above;

Y^3 and Y^4 are leaving groups;

W^1 and W^2 are selected from the group consisting of boronic acid groups [B(OH)$_2$], boronate ester groups of formula $B(OR^{35})_2$ wherein R^{35} is selected from the group consisting of alkyl groups as defined above and aryl groups as defined above or the two R^{35} groups together represent a straight or branched chain alkylene group having from 2 to 10 carbon atoms, and boranes of formula $B(OR^{36})_2$ wherein R^{36} is selected from the group consisting of alkyl groups as defined above, aryl groups as defined above and aralkyl groups as defined above; and

n^1 is an integer greater than 3.

Typically, in the above, the leaving groups Y^3 and Y^4 may be bromine or iodine; the substituents W^1 and W^2 may be boronate ester groups of formula $B(OR^{35})_2$ wherein the two groups R^{35} together represent an alkylene group having from 2 to 6 carbon atoms such as a 2,3-dimethylbutylene group; the palladium catalyst may be tetrakis-(triphenylphosphine)palladium (0); the base may be tetra-alkylammonium hydroxide, most preferably tetraethylammonium hydroxide as described in WO 00/53656,

PCT/GB00/00771; the reaction may be performed in toluene containing sodium carbonate as the required base and Aliquat® as a phase-transfer catalyst.

Scheme 2 below shows two specific examples of a Suzuki polymerisation of the general type set out in Scheme 1 above.

Scheme 2
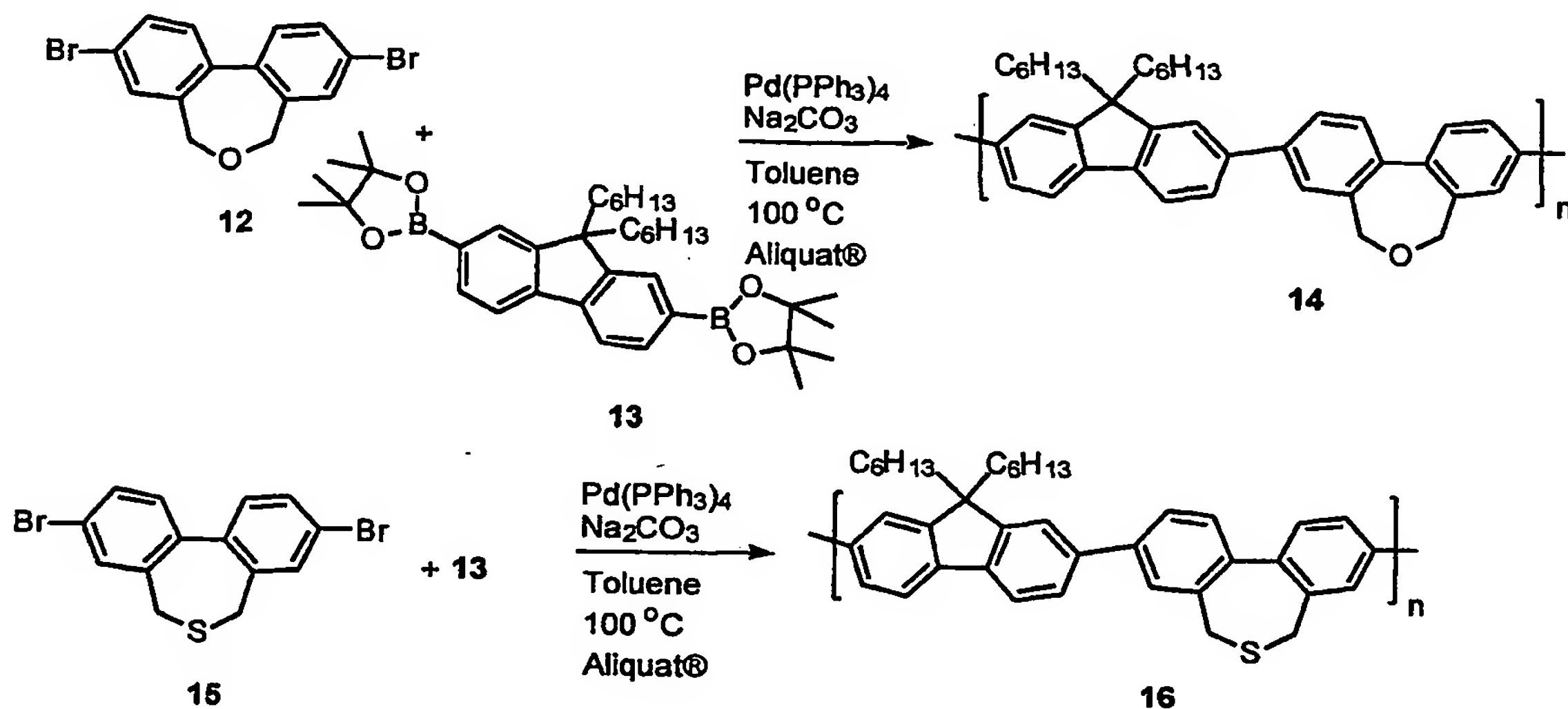
As already noted above, we particularly prefer statistical semiconductive copolymers comprising repeat units of formulae (I) and D^1. We have discovered a preferred method of synthesising such statistical copolymers which is a variation of the Suzuki polymerisation technique which enables the introduction of precise amounts of the repeat unit of formula (I) in a truly random manner along the polymer backbone. This has application not only in the present invention but also to the synthesis of other random statistical conjugated polymers.

Thus, in a further aspect of the present invention, there is provided a process for the preparation of a random statistical conjugated polymer comprising reacting, in the

presence of a palladium (0) or palladium (II) catalyst and a base, x^1 moles of a monomer of formula Y^5-F^1-Y^6, y^1 moles of W^3-F^1-W^4 and z^1 moles of a monomer of formula W^5-G^1-W^6, wherein Y^5 and Y^6 are leaving groups,

W^3, W^4, W^5 and W^6 are selected from the group consisting of boronic acid groups [$B(OH)_2$], boronate ester groups of formula $B(OR^{35})_2$ wherein R^{35} is as defined above and boranes of formula $B(OR^{36})_2$ wherein R^{36} is as defined above,

F^1 and G^1 are radicals the nature of which is such that, on polymerisation, the groups F^1 and G^1 in the resulting polymerisation product are conjugated, and

the molar ratio x^1:(y^1+z^1) is 1:1,

to give a random statistical conjugated polymer of formula (XVI) below wherein F^1, G^1, x^1, y^1 and z^1 are as defined above, the molar ratio (x^1+y^1):z^1 being greater than 1:

$$-\left(F^1\right)_{x^1+y^1} \sim\sim\sim \left(G^1\right)_{z^1}-$$
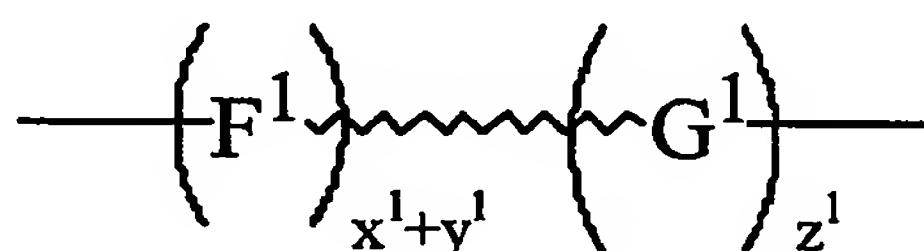
(XVI)

Typically, in the above, the leaving groups Y^5 and Y^6 may be bromine or iodine; the substituents W^3, W^4, W^5 and W^6 may each represent a boronate ester group of formula $B(OR^{35})_2$ wherein the two groups R^{35} in each boronate ester group together represent an alkylene group having from 2 to 6 carbon atoms such as a 2,3-dimethyl-butylene group; the palladium catalyst may be tetrakis(triphenylphosphine)palladium (0); and the reaction may be performed in toluene containing sodium carbonate as the required base and Aliquat® as a phase-transfer catalyst. Preferably the palladium catalyst is combined wiuth a tetraalkylammonium hydroxide base.

It has been surprisingly found that tricyclohexylphosphine in combination with palladium(II) acetate and tetraethylammonium hydroxide in toluene can lead to extremely rapid polymerisations and high molecular weight polymer. For the poly(9,9-dialkylfluorene-2,7-diyl) homopolymers typical M_p (as measured by GPC) in the range

200,000-350,000 were attained. Tri(*tert*-butylphosphine) may also be used. These specific phosphines were described by A. F. Littke and G. C. Fu, *J. Am. Chem. Soc.*, 2001, *123*, 6989 (and references cited therein) as suitable for efficient Suzuki coupling catalysts, but it is surprising that high molecular weight polymers are also accessible. Preferred stoichiometry includes 1 mol% palladium acetate, 3 mol% phosphine and 5 equivalents of tetraethylammonium hydroxide per mole of dibromoarene.
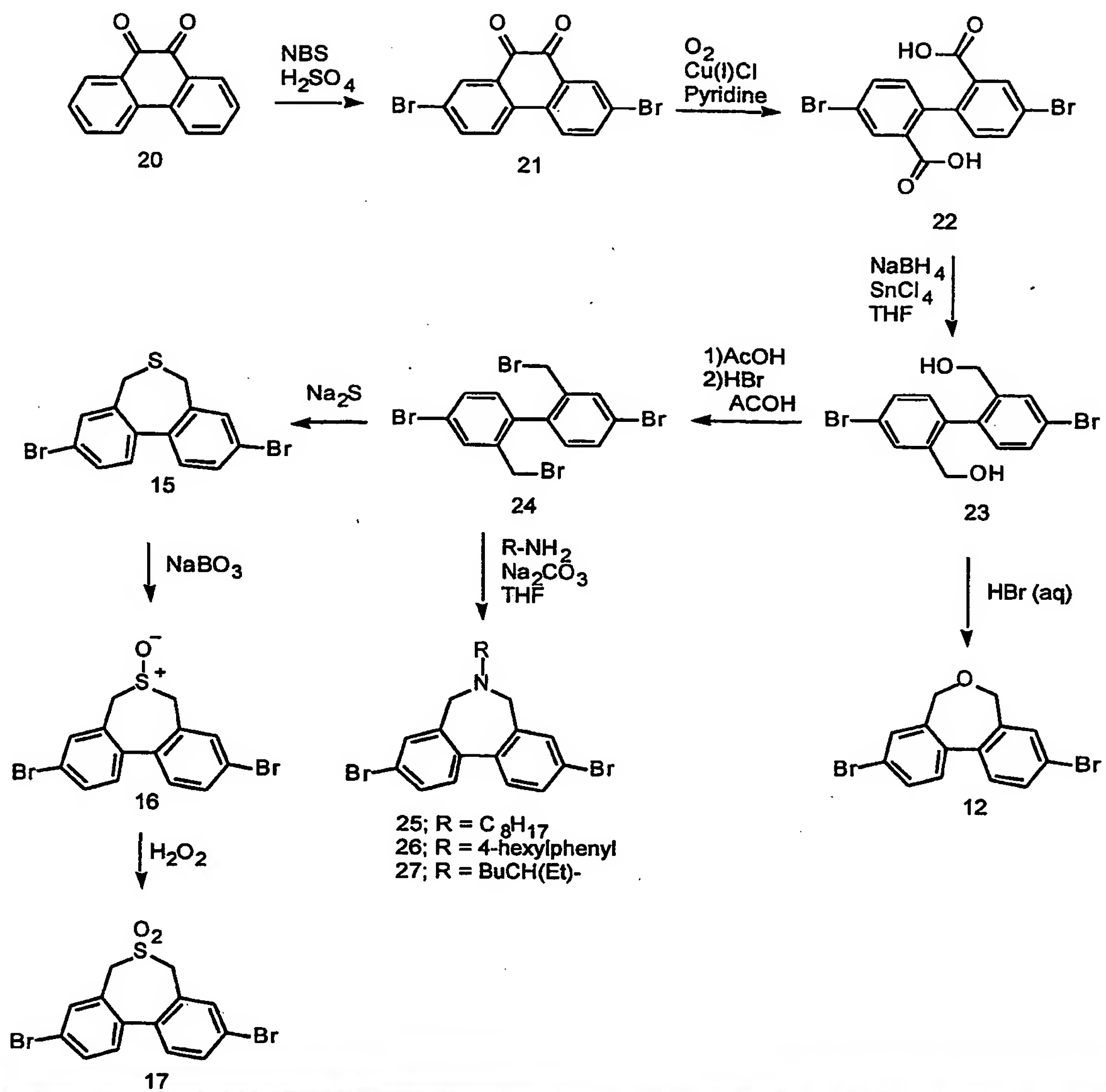
This modification of the Suzuki polymerisation technique is particularly useful as it enables truly random statistical copolymers to be formed in which small amounts of a desired monomer unit can be incorporated into the backbone of a polymer containing much larger amounts of the comonomer unit. In the specific example of the copolymers of the present invention, a copolymer of formula (VI) as defined above may be synthesised using the above method [in which method G^1 in the monomer W^5-G^1-W^6 is the repeat unit of formula (I) as defined above], said copolymer of formula (VI) having a molar proportion of the repeat unit D^1 which is much greater than that of the repeat unit of formula (I), allowing small amounts of twisting to be introduced along the polymer backbone. This random introduction of small amounts of the repeat unit (I) allows control over the degree of reduction of conjugation in the polymer produced by the introduction of said repeat unit of formula (I). As a consequence, the change in the HOMO-LUMO bandgap can be tailored as required to produce the desired blue-shift in the polymer emission, and the degree to which aggregation of the polymers is reduced can be similarly tuned.
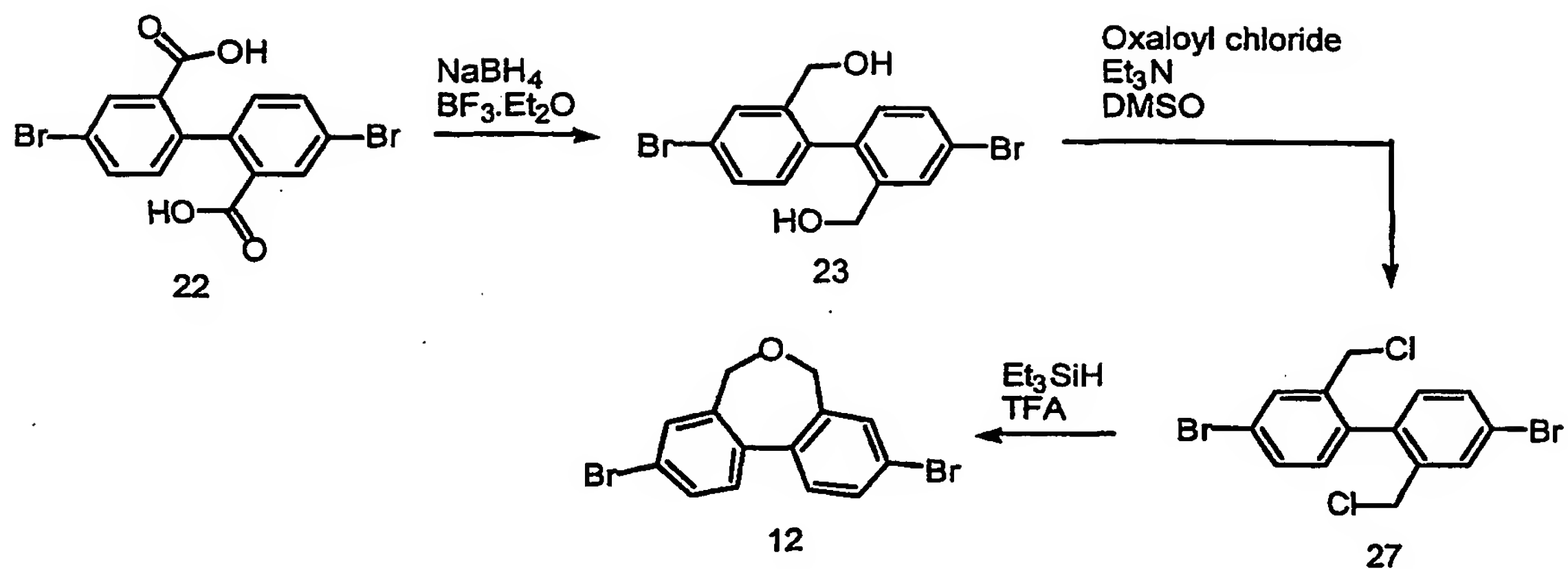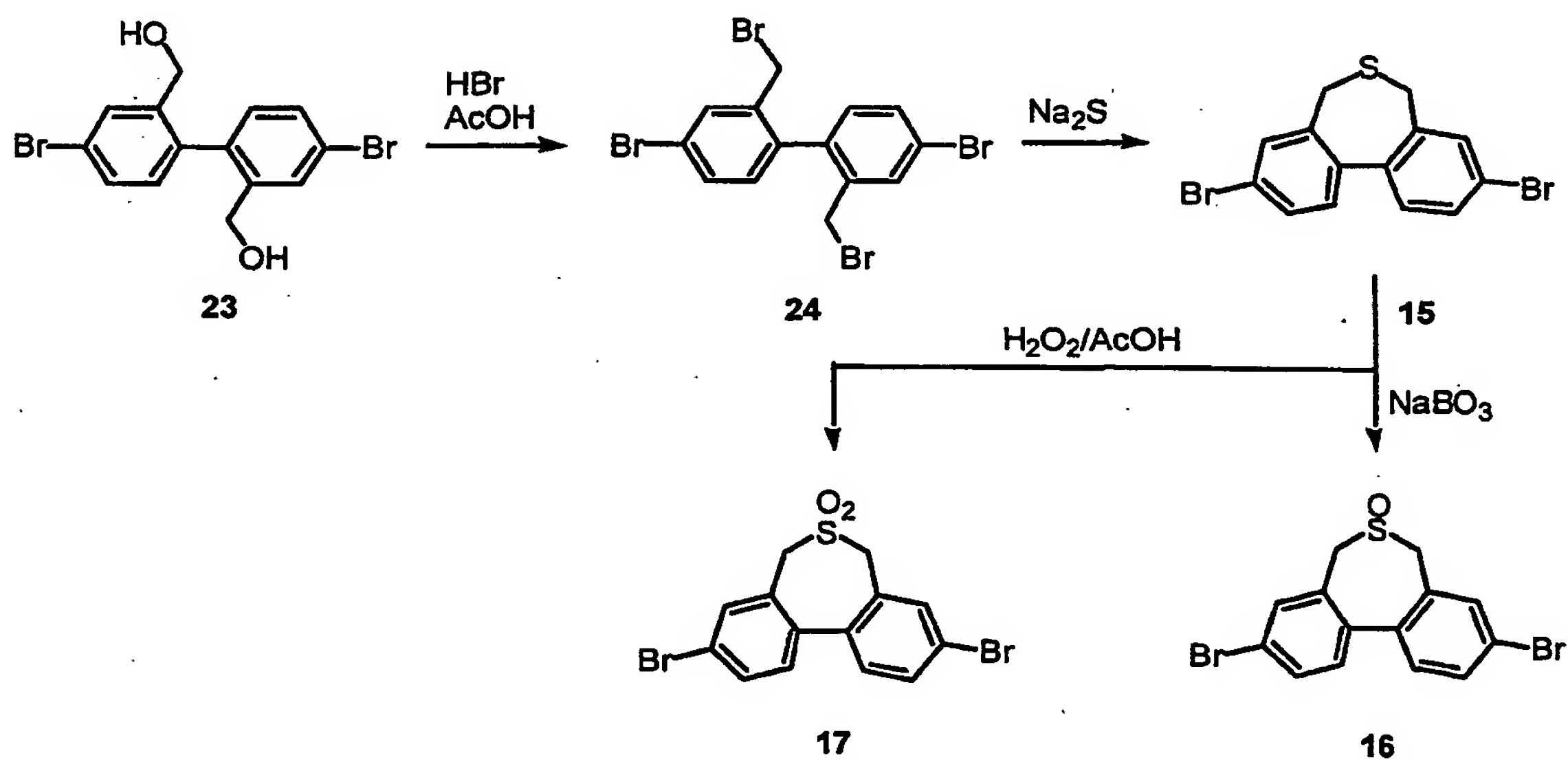
A further example of a suitable polymerisation technique is a Horner-Emmons polycondensation of a phosphonate with an aldehyde, as illustrated below in Scheme 3.
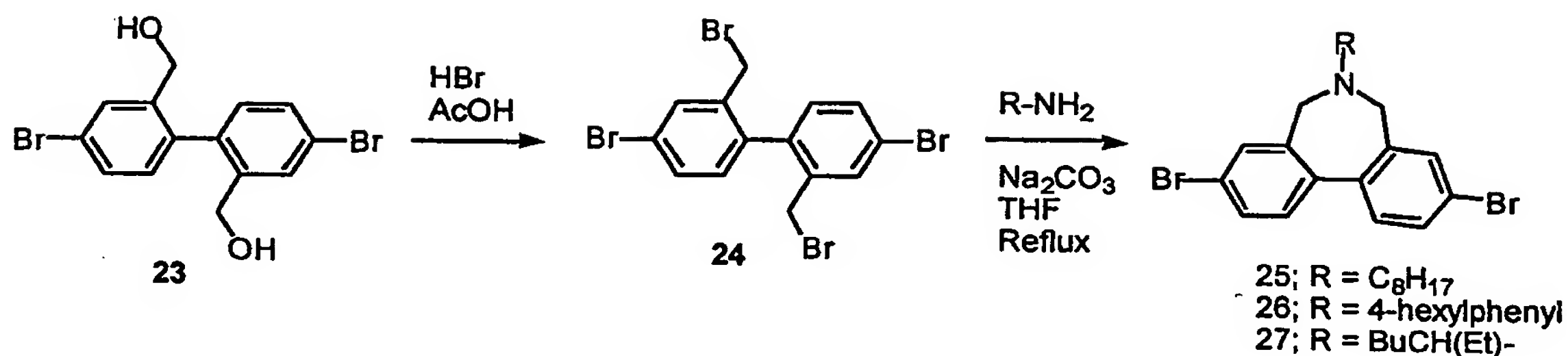
Scheme 3
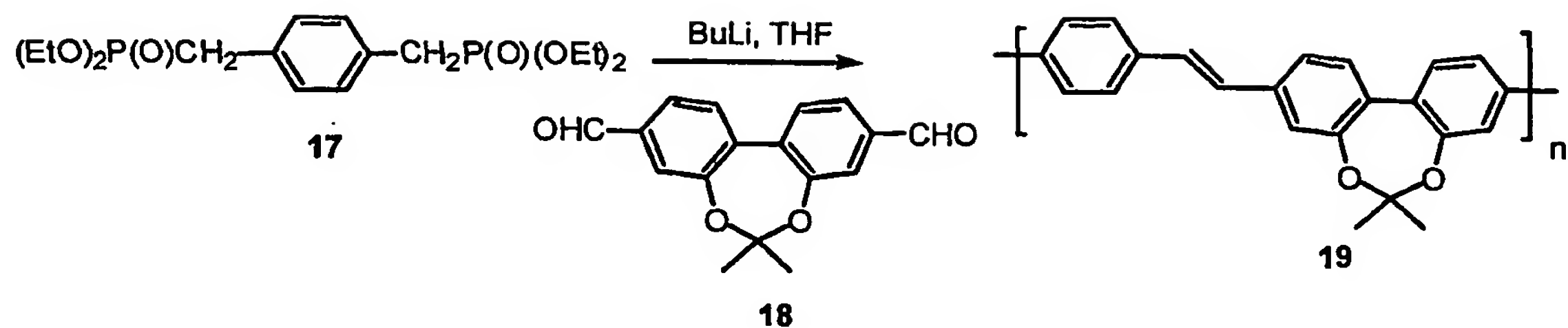
In the polymerisation techniques described above, end-capping units may be introduced if required, e.g. by the addition of aryl bromides or aryl boronates after a predetermined time to prevent further chain extension of the polymers.

The twisted monomers of the present invention of formulae Y^3-E-Y^4 and W^1-E-W^2 as defined above can be synthesised according to standard techniques well known in the field of synthetic organic chemistry. Examples of such techniques are illustrated in the following Schemes 4 to 7.

Scheme 4

NBS
H₂SO₄

O₂
Cu(I)Cl
Pyridine

NaBH₄
SnCl₄
THF

1)AcOH
2)HBr
ACOH

Na₂S

NaBO₃

R-NH₂
Na₂CO₃
THF

HBr (aq)

H₂O₂

20

21

22

23

24

15

16

12

17

25; R = C₈H₁₇
26; R = 4-hexylphenyl
27; R = BuCH(Et)-

Scheme 5

Scheme 6

Scheme 7

25; R = C₈H₁₇
26; R = 4-hexylphenyl
27; R = BuCH(Et)-

Many of the monomers used in the above polymerisation reactions are novel. In a further aspect of the present invention there are provided monomers of formulae Y^3-E-Y^4 and W^1-E-W^2, wherein E, W^1, W^2, Y^3 and Y^4 are as defined above, provided that, where each of Y^3 and Y^4 is a bromine atom, E does not represent a dibenzoxepinyl, dibenzothiepinyl, dibenzothiepinyl S-oxide or dibenzothiepinyl S,S-dioxide group.

The optical devices of the present invention may be prepared according to any method known in this field for the preparation of optical devices. Suitable preparation methods are disclosed in, for example, the following, the contents of which are incorporated herein by reference thereto: WO-A-90/13148; US-A-5,512,654; WO-A-95/06400; R.F. Service, *Science* 1998, *279*, 1135; Wudl et al., *Appl. Phys. Lett.* 1998, *73*, 2561; J. Bharathan, Y. Yang, *Appl. Phys. Lett.* 1998, *72*, 2660; and T.R. Hebner, C.C. Wu, D. Marcy, M.L. Lu, J. Sturm, *Appl. Phys. Lett.* 1998, *72*, 519).

As an example, a typical thin-film LED optical device according to the present invention comprises O_2 plasma-treated ITO-coated glass, a poly(styrene sulfonate)-doped poly (3,4-ethylene dioxythiophene) (PEDOT:PSS) hole injection layer, a thin film of a semiconductive copolymer of the present invention, and a Ca-Al cathode. The PEDOT:PSS films (typically approximately 70 nm in thickness) can be spun from a filtered H_2O solution before heating to 100°C under N_2 for 30 minutes. Spin-coating can also be also used to deposit the emissive copolymer films of the present invention (typically approximately 100 nm in thickness) from xylene solutions in a nitrogen-filled glove box. The Ca cathode (typically approximately 500 Å in thickness) and Al

protective layers (typically approximately 150 Å in thickness) can be deposited by thermal evaporation in a vacuum (e.g. base pressure approximately 5×10^{-6} mbar) patterned by a shadow mask.

Water soluble and polyelectrolyte copolymers according to the present invention may be prepared by the copolymerisation of ammonium salts with suitable fluorene monomers. Selection of suitable polymers could be advantageous for inkjet printing as well as layer by layer deposition of light emitting polyelectrolytes.

The present invention may be further understood by consideration of the following embodiments of the present invention, with reference to the following drawings in which:

Figure 1 shows the X-ray crystal structure of a twisted monomer **12** prepared in Example 1 below;

Figure 2 shows UV/VIS solution spectra for various semiconductive polymers of general formula **33** prepared in Example 2 below;

Figure 3 shows thin film photoluminescence spectra for a semiconductive polymer of general formula **33** prepared in Example 2 below and two prior art copolymers;

Figure 4 shows a current-voltage photoluminescence curve for a two layer electroluminescent device incorporating a semiconductive statistical copolymer of formula **36** prepared in Example 3 below; and

Figure 5 shows a schematic diagram of an electroluminescent device of the present invention.

Figure 6 Thin film photoluminescence spectra for the designated copolymers (excitation wavelength 360 nm)

Figure 7 Thin film photoluminescence spectra for the designated copolymers (excitation wavelength 360 nm).

Figure 8 Thin film photoluminescence spectra for the designated copolymers (excitation wavelength 360 nm).

Figure 9 Thin film photoluminescence spectra for the designated copolymers (excitation wavelength 360 nm).

Figure 10 Electroluminescence spectrum for the PF6 copolymer **36** (m = 75; n = 25) shown in the attached figure. Device construction was according to the procedure outlined in this document.

Example 1

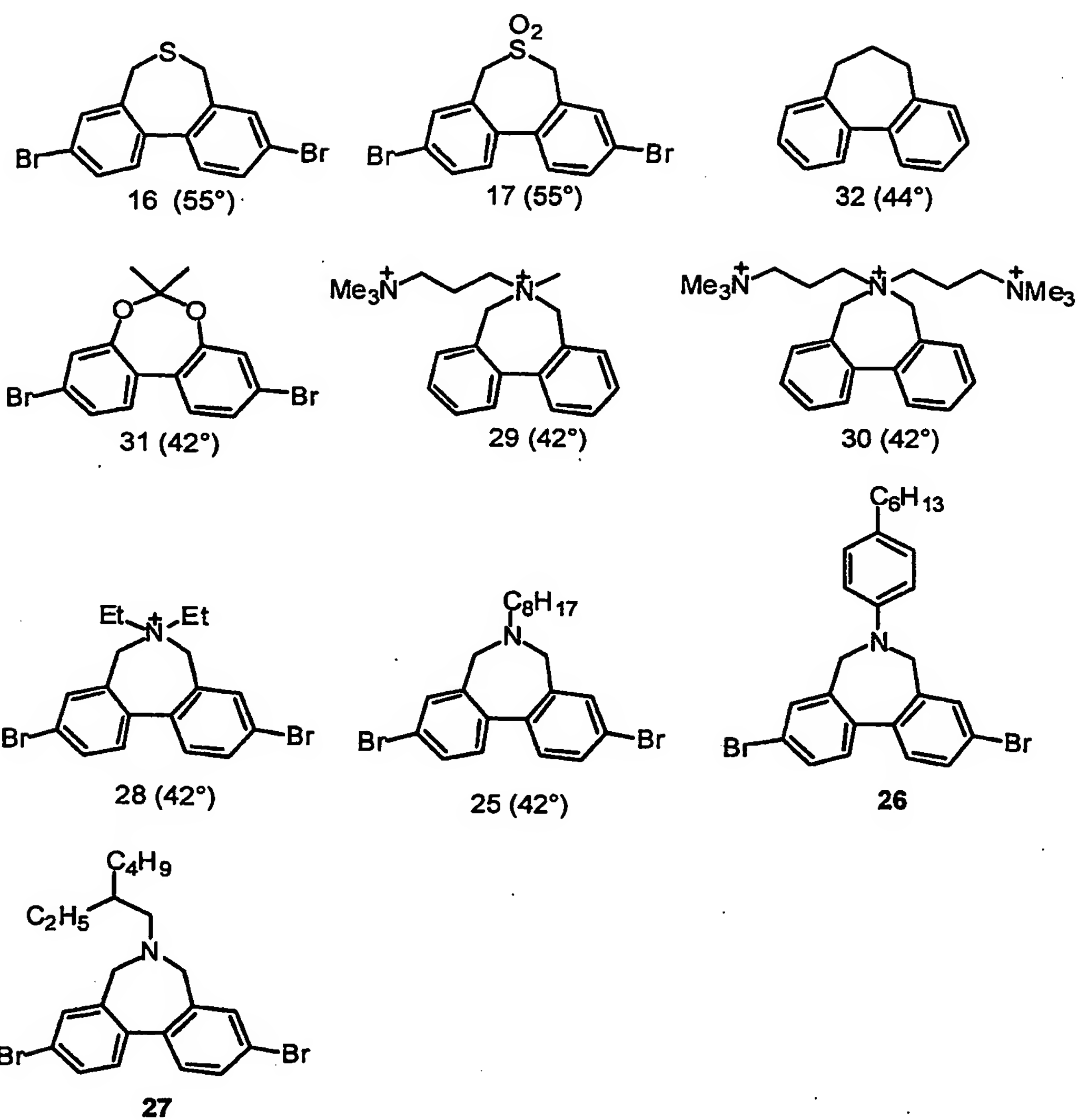## Synthesis of 3,9-dibromo-5,7-dihydro-dibenz[c, e]oxepin (7)
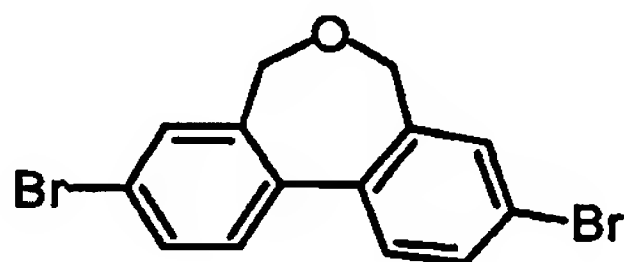
12

4,4'-Dibromo-2,2'-bis-hydroxymethyl-biphenyl **23**, the structure of which is shown in Scheme 4 above, (5 g, 0.013 moles, prepared according to the procedure described by D. M. Hall, F. Minhaj, *J. Chem. Soc.*, 1957, 4584) was dissolved in THF (50 ml). HBr (48 % wt/wt aqueous solution, 40 ml) was added and the solution refluxed overnight. After this period the THF was removed under reduced pressure and the yellow oil extracted between DCM/H_2O (DCM is dichloromethane). The combined organic layers were dried ($MgSO_4$), reduced and recrystallised from acetone (100 ml) to yield 3,9-dibromo-5,7-dihydro-dibenz[c, e]oxepin (**12**) as fine white crystals (1 g). Repeated recrystallisations of the mother liquor gave further product. Total yield after 3 recrystallisations (2.2 g, 0.0062 moles, 48 % yield) as fine white crystals.

^{1}H-NMR (400 MHz, $CDCl_3$): 4.30 (4H, s, CH_2), 7.39 (2H, d, ArH, J 8), 7.58-7.63 (4H, m, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) 67.0, 122.4, 128.9, 132.1, 132.7, 136.8, 139.0; Elemental analysis (calculated for $C_{14}H_{10}Br_2O$, C 47.50, H 2.85 %); found: C 47.44, H 2.94 %;

mp. 129-131 °C.

The X-ray crystal structure of 3,9-dibromo-5,7-dihydro-dibenz[c, e]oxepin (12) thus prepared was obtained using single crystal X-ray crystallography and this is shown in Figure 1. From this it was possible to measure that there is a torsion angle about the biphenyl linkage of 41.25° between the phenyl rings.

Using similar synthetic methodology as described above for the preparation of 3,9-dibromo-5,7-dihydro-dibenz[c, e]oxepin, the further twisted monomers **15, 17, 25-32** shown below have been prepared. The torsion angle for many monomers has been measured as for 3,9-dibromo-5,7-dihydro-dibenz[c, e]oxepin, and the values are shown in brackets after each number. It should be noted that **29, 30,** and **32** were not converted to the dibromo derivatives, but the potential for exploitation in cross-coupling reactions is evident.

16 (55°)

17 (55°)

32 (44°)

31 (42°)

29 (42°)

30 (42°)

28 (42°)

25 (42°)

26

27

Torsion angles from X-ray crystal structures of selected monomers

33

Example 2

Statistical polymerisation of 3,9-dibromo-5,7-dihydro-dibenz[c, e]oxepin (12) with 9,9-di-n-hexylfluorene-2,7-bis-(isopropoxy-4,4,5,5-tetra-methyl-1,3,2-dioxaboronate) 13 and 2,7-dibromo-9,9-di-n-hexylfluorene

9,9-Di-n-hexylfluorene-2,7-bis-(isopropoxy-4,4,5,5-tetra-methyl-1,3,2-dioxaboronate) (structure **13** below) (1.84 g, 3.13 mmol), 2,7-dibromo-9,9-di-n-hexylfluorene (154 mg, 0.313 mmol) and 3,9-dibromo-5,7-dihydro-dibenz[c, e]oxepin **12** (1 g, 2.82 mmol), prepared as described in Example 1 above, were placed in a flame dried Schlenk tube under nitrogen. Tetrakis(triphenylphosphine)palladium (0) (40 mg, 0.03 mmol), toluene (40 ml), aqueous sodium carbonate (6 ml, 2 M) and Aliquat® (120 mg) were then added and the solution degassed. The resulting mixture was heated to 100 °C for 48 hours under nitrogen. The resulting viscous liquid was then precipitated in methanol to give an off-white solid. The polymer was finally re precipitated from a filtered toluene solution into methanol to give poly (9,9-dialkylfluorene)-co-(5,7-dihydro-dibenz[c, e]oxepin) (structure **33** below: 55 % fluorene, and 45 % structural unit derived from **12**).

Conventional calibration GPC (PS standards, 30 °C) Mn 12 K, MWD 5, bimodal);

^{1}H-NMR (250 MHz, CDCl$_3$) 0.80 (br, 10H, CH$_3$+CH$_2$), 1.12 (br, 12H, CH$_2$), 2.12 (br, 4H, CH$_2$), 4.50 (br, 3.6H, CH$_2$, 45 % of 4H CH$_2$ signal of methylene groups adjacent to the aromatic ring in hexyl substituents in relation to 4H signal at 2.12 ppm), 7.50-7.87 (12H, Ar-H);
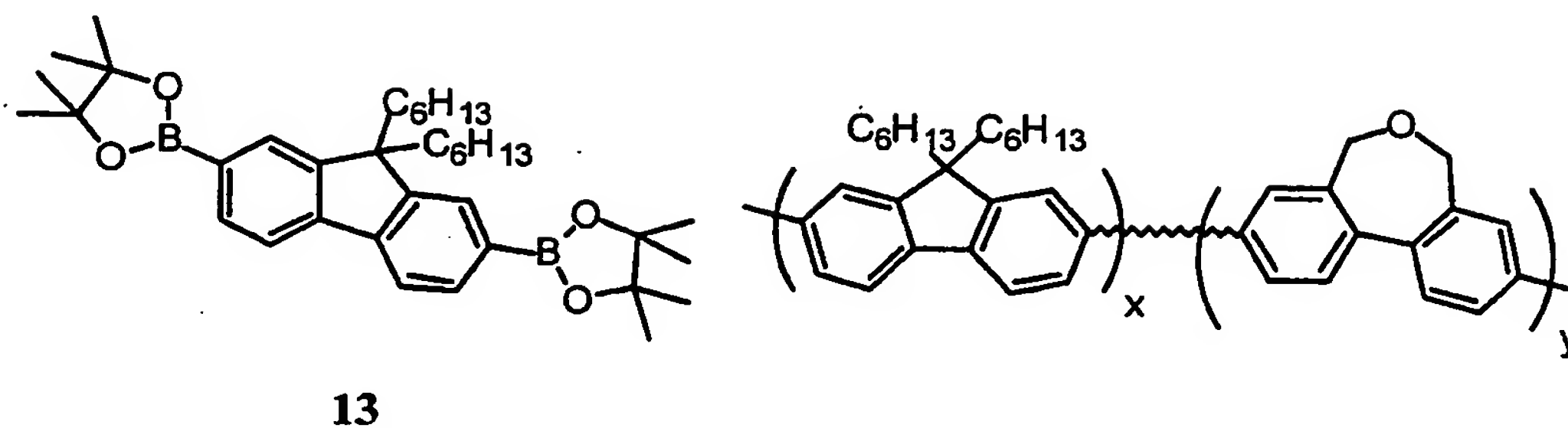
Solution UV (methylenechloride, RT) λ$_{max}$ 366 nm;

Thin film UV λ$_{max}$ 372 nm;

Cylic voltammetry (Ag/AgCl corrected with iron (II) ferrocene) E$_{ox}$ 1.46 V, E$_{red}$ -0.84 V E$_{ox}$-E$_{red}$ 2.3 eV;

PL Spectra (methylene chloride) λ$_{max}$ 412 nm, λ$_{max}$ (shoulder) 445 nm;

PL spectra λ$_{max}$ 418nm, λ$_{max}$ (shoulder) 450 nm.

C$_6$H$_{13}$ C$_6$H$_{13}$

13

C$_6$H$_{13}$ C$_6$H$_{13}$

Structure **33** (x = 55 %, y = 45 %)

By varying the relative amounts of 9,9-di-n-hexylfluorene-2-(isopropoxy-4,4,5,5-tetra-methyl-1,3,2-dioxaboronate), 2,7-dibromo-9,9-di-n-hexylfluorene and 3,9-dibromo-5,7-dihydro-dibenz[c, e]oxepin used in the above polymerisation technique, a series of statistical copolymers shown in Table 1 below were prepared [the polymer having 0% of **B** is, of course, the homopolymer poly(di-n-hexylfluorene)].

Table 1

C$_6$H$_{13}$ C$_6$H$_{13}$

33
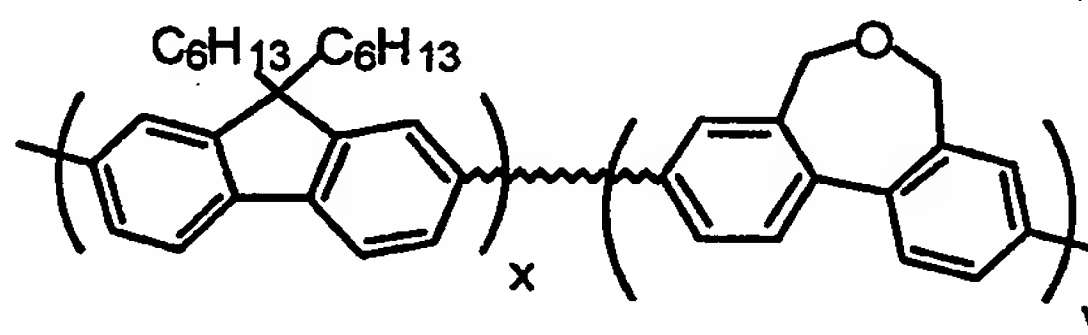
A	B
Polymer Composition (%)	
A	B
100	0
90	10
75	25
65	35
55	45
50	50

The solution UV/VIS absorption spectra of these polymers **33** were obtained and are illustrated in Figure 2 (in this figure, the term "ether" refers to the twisted monomer unit of structure **B** in **33**). As can be seen, a blue shifted emission was obtained in the copolymers of the present invention, the shift increasing with increasing amount of twisted monomer unit of structure **B**.

The UV/VIS absorption spectra for the statistical copolymer of formula **33** having 25% of unit **B** and 75% of unit **A** was compared with the spectra for poly (di-n-hexylfluorene) having the structure **34** below and a copolymer having the structure **35** below containing 75% 9,9-di-n-hexylfluorenyl groups and 25% phenyl groups (see Figure 3). As can be seen, the statistical copolymer of the present invention has a considerably reduced long wavelength tail in the visible region when compared with the two prior art polymers.

34

35
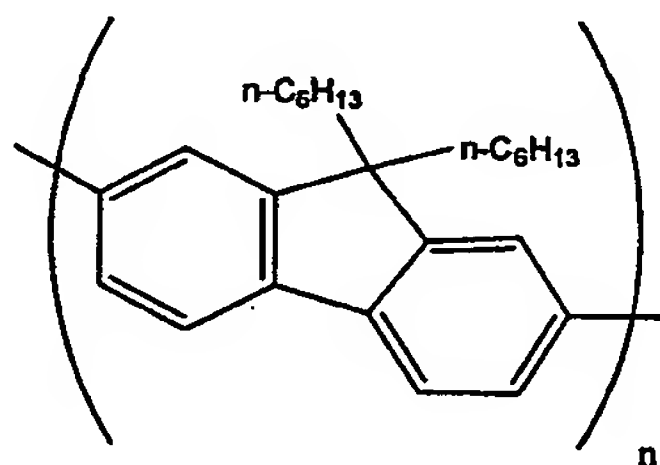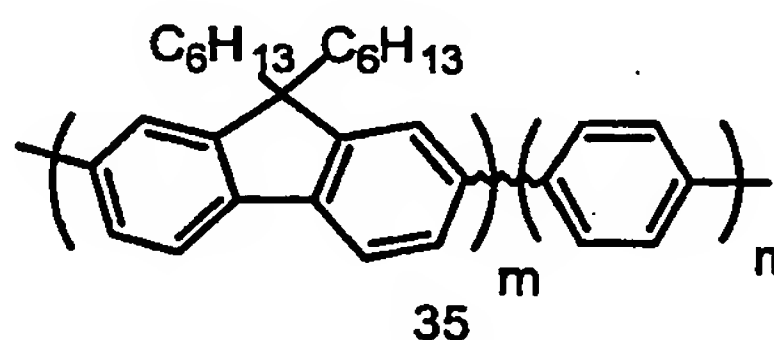
m:n = 3:1

The photoluminescence spectra of the copolymers of this example were measured and are shown in Figure 4 (in dichloromethane) and Figure 5 (thin film). As the amount

of 5,7-dihydro-dibenz[c, e]oxepin decreases, the emission is shifted to longer wavelength. Additonally, cyclic voltammetry data for the copolymers were measured, the results of which are as follows.

Polymer	Eox (V)	Ered (V)	Band Gap (eV)	Homo (eV)	Lumo (eV)
PF6	1.36	-0.91	2.3	-6.2	-3.9
10% B	1.33	-0.97	2.3	-7.5	-3.8
25% B	1.34	-0.93	2.3	-6.1	-3.9
35% B	1.54	-0.89	2.4	-6.3	-3.9
45% B	1.46	-0.84	2.3	-6.3	-4.0
50% B	1.47	-0.82	2.3	-6.3	-4.0

1   40mV/s sweep rate
2   MeCN solvent, 0.1M tetraalkylammonium tetrafluoroborate electrolyte
3   Polymers studied as thin films spun from toluene solution
4   This band gap corresponds to light of wavelength 540nm (green)
5   Values are against Ag/AgCl corrected with FOC (0.43 V)

Example 3

Statistical polymerisation of 3,9-dibromo-5,7-dihydro-dibenz[c, e]thiepin (15) with 9,9-di-n-hexylfluorene-2,7-bis-(isopropoxy-4,4,5,5-tetra-methyl-1,3,2-dioxaboronate) 13

To a solution of 3,9-dibromo-5,7-dihydro-dibenz[c, e]thiepin **15** (0.37 g, 1.00 mmol, 1 equivalent) and 9,9-di-n-hexylfluorene-2,7-bis-(isopropoxy-4,4,5,5-tetra-methyl-1,3,2-dioxaboronate) **13** (0.50 g, 1.00 mmol, 1 eq.) in dry degassed tetrahydrofuran (30 ml) (degassing was achieved by three pump-freeze-thaw cycles) was added a solution of Cs_2CO_3 (3.3 g in 5 ml H_2O, 2 M) and tetrakis(triphenylphosphine) palladium(0) (0.021 g, 0.02 mmol, 0.02 equivalents) under an atmosphere of nitrogen. After heating to reflux for 4 days, the concentrated polymer solution was filtered through a short silica plug (pasteur pipette) and then precipitated from methanol (500 ml). After drying the title

polymer **36** was obtained in 32% yield as a white solid (0.18 g); v_{max} (CHCl$_3$) / cm^{-1}

3037, 2931, 2860, 2393, 1605, 1465, 1262, 1003, 820; δ_H (500 MHz; CDCl$_3$): 7.85-7.38

(12 H, m, ArH), 3.76 (2 H, br s, SCH$_2$), 3.52 (2 H, br s, SCH$_2$), 2.10 (4 H, br s,

ArC(C*H$_2$*C$_5$H$_{11}$)$_2$), 1.22-1.05 (12 H, br s, alkyl), 0.83-0.64 (10 H, m, alkyl);   GPC

(CHCl$_3$) M_w 1.4 · 10^4, M_n 4.3 · 10^3, M_w/M_n 3.3; TGA: 391 °C (5% weight loss); λ_{max}

(CHCl$_3$)/nm 356.
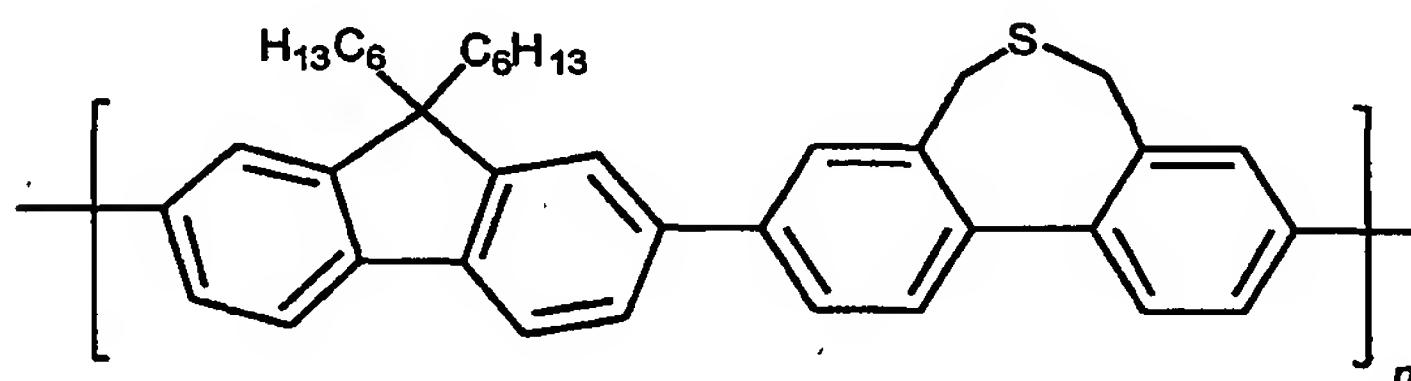
$$M_n = 4300$$
$$M_w = 14300$$
$$M_w / M_n = 3.32$$

36

Example 4
Preparation of an Electroluminescent Device

An indium-tin oxide (ITO) coated glass substrate was patterned in stripes (3 mm

in width) and washed with water, acetone and ethanol. A hole-injection layer, Poly(3,4-

ethylene-dioxythiophene):poly(styrene sulfonic acid) (PEDT:PSS), was spin-coated

(2000 rpm, 30 seconds) onto the ITO. The PEDT:PSS layer was dried on a hotplate (130

°C) for 5 minutes. Next, the light-emitting polymer F prepared in Example 3 above was

spin-coated on top of the PEDT:PSS layer. Then, the device was transferred to a high-

vacuum coating unit and set with a shadow mask (2 mm stripes). A cathode metal,

calcium, was deposited on the organic layers through the shadow mask, followed by

deposition of aluminium. The size of each pixel is 3 mm x 2 mm. The device was finally

encapsulated to keep out moisture. The deposition was carried out under high vacuum (1

x 10^{-5} mbar).Generally, PEDT:PSS is provided as aqueous solution, and light-emitting

polymers are prepared as solutions in organic solvent. Low workfunction metals are normally used as a cathode. The typical thicknesses of the layers are as follows: ITO (190 nm) / PEDT:PSS (50 nm) / light-emitting polymer (60 nm) / Ca (40 nm) / Al (200 nm). The devices were examined by applying d.c. bias (0 to 30 V) to the electrodes. The electroluminescent characteristics were measured with a Hewlett-Packard E3631A DC Power Supply, Keithley 2000 Digital Multimeter, Topcon BM-8 Luminance Meter, and Aminco-Bowman. A schematic diagram depicting the structure of the device is shown in Figure 7 (PF in this diagram refers to the copolymer F of Example 3). A further device, which was prepared almost identically to above, but in which the Ca layer was excluded, was also prepared.

Various physical characteristics of the devices thus prepared were measured and are set out below in Table 2.

Table 2
Data for polymer 36

Name		HTL pedt-nm	thick (nm)	Max lum (Cd/m^2)	@ V (V)	@ J (mA/ cm^2)	Max iqe. (%)	Max lm/W	Max Cd/A	Von (V) (10 mCd/m^2)
fcm01.	Ca-Al	50	60	20.24	7	168.8	0.04196	0.005373	0.01199	3.8-5
fcm02.	Al	50	60	0.5253	8.5	646.7	0.00044	3e-05	8.12e-05	6.4

HTL = hole transport layer
thick = thickness of LEP layer
max lum = maximum luminescence efficiency
@V = voltage to achieve maximum luminescence
@J = current density
max iqe = maximum internal quantum efficiency

A current voltage luminescence curve for the fcm01 device above is shown in Figure 6.

Claims

1. An optical device comprising a substrate and at least one semiconductive polymer supported by said substrate, wherein said semiconductive polymer is a copolymer in which one of the repeat units is a group of formula (I) below or a homopolymer in which the repeat unit is a group of formula (I) below:


(I)
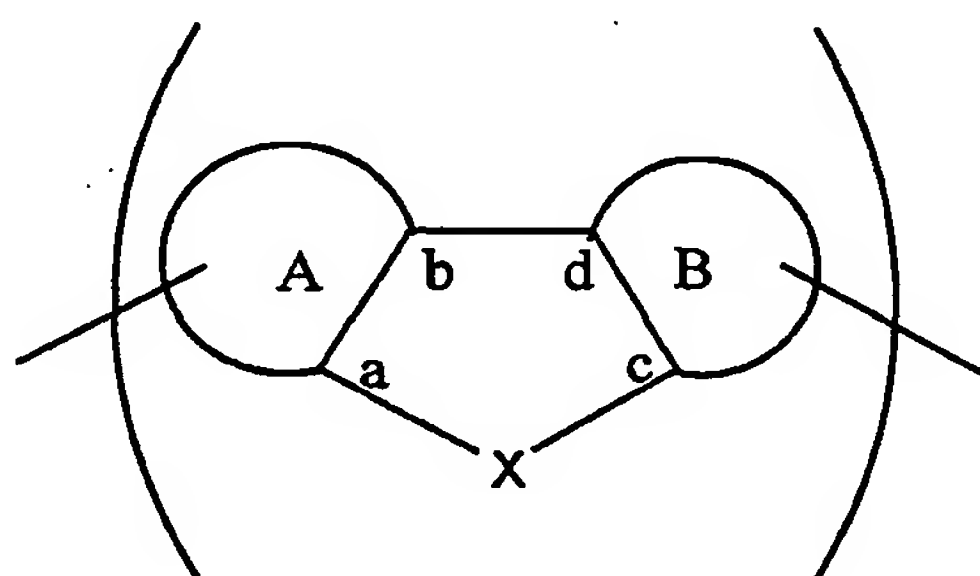
wherein:

A and B are the same or different and each comprises wholly or partially an aryl moiety or a heteroaryl moiety, said moiety in A being fused to the bond a-b and said moiety in B being fused to the bond c-d; and

X is a linking unit, X being such that there is a torsion angle of at least 5° between the bond a-b and the bond c-d about the bond b-d.

2. An optical device according to claim 1, wherein the torsion angle between the bond a-b and the bond c-d about the bond b-d is from 5° to 75°.

3. An optical device according to claim 1, wherein the torsion angle between the bond a-b and the bond c-d about the bond b-d is from 10° to 70°.

4. An optical device according to claim 1, wherein the torsion angle between the bond a-b and the bond c-d about the bond b-d is from 30° to 60°.

5.   An optical device according to claim 1, wherein the torsion angle between the bond a-b and the bond c-d about the bond b-d is from 40° to 55°.

6.   An optical device according to any one of claims 1 to 5, wherein said aryl moiety is an aromatic hydrocarbon moeity having from 6 to 14 carbon atoms in one or more rings which may optionally be substituted with at least one substituent selected from the group consisting of nitro groups, cyano groups, amino groups, alkyl groups defined below, haloalkyl groups defined below, alkoxyalkyl groups defined below, aryloxy groups defined below and alkoxy groups defined below;

the alkyl groups above are straight or branched-chain alkyl groups having from 1 to 20 carbon atoms;

the haloalkyl groups above are alkyl groups as defined above which are substituted with at least one halogen atom;

the alkoxy groups above are straight or branched-chain alkoxy groups having from 1 to 20 carbon atoms;

the alkoxyalkyl groups above are alkyl groups as defined above which are substituted with at least one alkoxy group as defined above; and

the aryl moiety of the aryloxy groups above is an aromatic hydrocarbon group having from 6 to 14 carbon atoms in one or more rings which may optionally be substituted with at least one substituent selected from the group consisting of nitro groups, cyano groups, amino groups, alkyl groups as defined above, haloalkyl groups as defined above, alkoxyalkyl groups as defined above and alkoxy groups as defined above.

7.   An optical device according to any one of claims 1 to 6, wherein said heteroaryl moiety is a 5- to 7-membered aromatic heterocyclic moiety containing from 1 to 3 heteroatoms selected from the group consisting of sulfur atoms, oxygen atoms and nitrogen atoms, said moiety optionally being substituted with at least one substituent selected from the group consisting of nitro groups, cyano groups, amino groups, alkyl groups as defined in claim 6, haloalkyl groups as defined in claim 6, alkoxyalkyl groups as defined in claim 6, aryloxy groups as defined in claim 6 and alkoxy groups as defined in claim 6.

8.   An optical device according to claim 1, wherein said repeat unit of formula (I) is a group of formula (II) below:
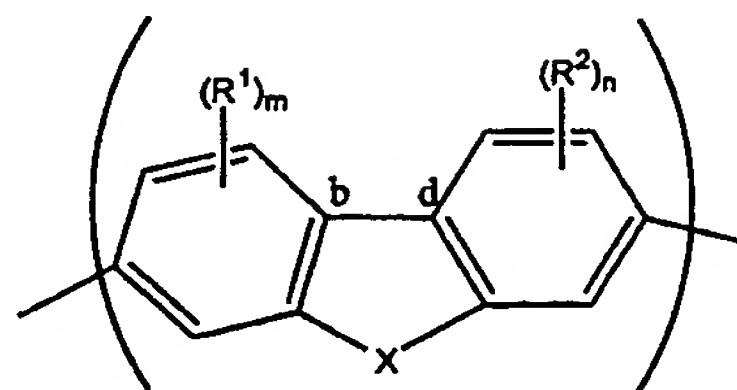

(II)
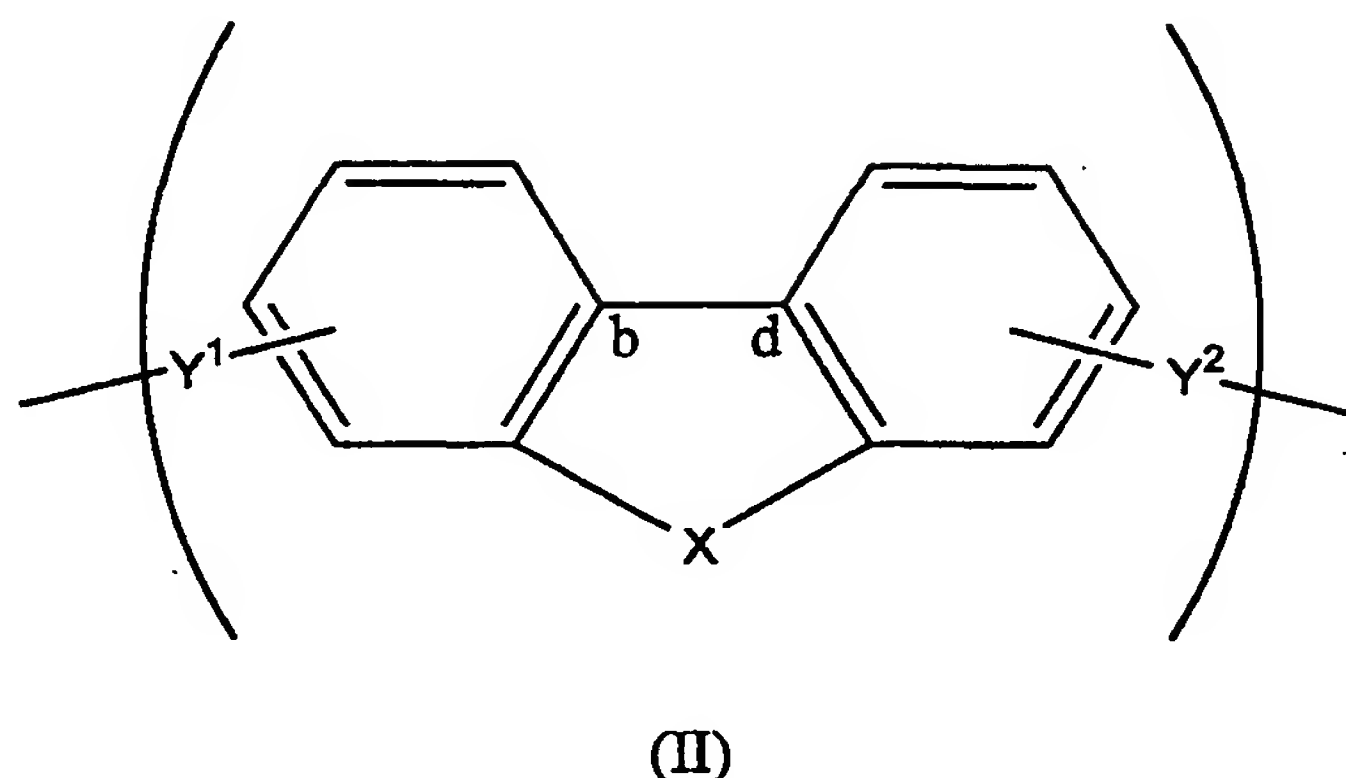
wherein:

Y^1 and Y^2 are the same or different and each represents a single bond or a linking unit that is conjugated with the phenyl group to which it is attached; and

X is a linking unit, X being such that there is a torsion angle of at least 5° between the two phenyl groups about the bond b-d.

9.   An optical device according to claim 8, wherein Y^1 and Y^2 are the same or different and are selected from a phenyl group (which is fused with the phenyl group of the group of formula (II) to which it is attached to form a naphthylene linking unit) and an indenyl group (which is fused with the phenyl group of the group of formula (II) to which they it is attached to form a fluorenyl linking unit).

10.   An optical device according to claim 8, wherein each of Y^1 and Y^2 is a single bond.

11.   An optical device according to claim 1, wherein said repeat unit of formula (I) is a group of formula (III) below:

(III)

wherein:

m and n are the same or different and each is 0 or an integer of 1, 2 or 3;

R^1 and R^2 are same or different and each is selected from the group consisting of alkyl groups as defined in claim 6, haloalkyl groups as defined in claim 6, alkoxy groups as defined in claim 6, alkoxyalkyl groups as defined in claim 6, aryl groups (comprising aromatic hydrocarbon groups having from 6 to 14 carbon atoms in one or more rings which may optionally be substituted with at least one substituent selected from the group consisting of nitro groups, cyano groups, amino groups, alkyl groups as defined in claim 6, haloalkyl groups as defined in claim 6, alkoxyalkyl groups as defined in claim 6 and alkoxy groups as defined in claim 6), aryloxy groups as defined in claim 6, and aralkyl groups comprising an alkyl group as defined in claim 6 which is substituted with at least one aryl group as defined above; and

X is a linking unit, X being such that there is a torsion angle of at least 5° between the two phenyl rings about the bond b-d.

12.   An optical device according to claim 11, wherein X is a moiety of formula -A-B-C- wherein A, B and C are the same or different and each is selected from the group consisting of O, S, SO, SO_2, NR^3, $N^+(R^{3'})(R^{3''})$, $C(R^4)(R^5)$, $Si(R^{4'})(R^{5'})$, and $P(O)(OR^6)$, wherein:

R^3, $R^{3'}$ and $R^{3''}$ are the same or different and each is selected from the group consisting of hydrogen atoms, alkyl groups as defined in claim 6, haloalkyl groups as

defined in claim 6, alkoxy groups as defined in claim 6, alkoxyalkyl groups as defined in claim 6, aryl groups as defined in claim 11, aryloxy groups as defined in claim 6, aralkyl groups as defined in claim 11, and alkyl groups as defined in claim 11 which are substituted with at least one group of formula $-N^+(R^7)_3$ wherein each group R^7 is the same or different and is selected from the group consisting of hydrogen atoms, alkyl groups as defined in claim 6 and aryl groups as defined in claim 11;

R^4, R^5, $R^{4'}$ and $R^{5'}$ are the same or different and each is selected from the group consisting of hydrogen atoms, alkyl groups as defined in claim 6, haloalkyl groups as defined in claim 6, alkoxy groups as defined in claim 6, halogen atoms, nitro groups, cyano groups, alkoxyalkyl groups as defined in claim 6, aryl groups as defined in claim 11, aryloxy groups as defined in claim 6, aralkyl groups as defined in claim 11 and alkyl groups as defined in claim 6 which are substituted with a substituent selected from the group consisting of aryl groups as defined in claim 11, heteroaryl groups as defined below, fluorenyl groups and spirobifluorenyl groups, said aryl, heteroaryl, fluorenyl and spirobifluorenyl groups being substituted with a disubstituted amino group the substituents of which are the same or different and are selected from the group consisting of aryl groups as defined in claim 11, heteroaryl groups as defined below, fluorenyl groups and spirobifluorenyl groups, or R^4 and R^5 together with the carbon atom to which they are attached represent a carbonyl group; and

R^6 is selected from the group consisting of hydrogen atoms, alkyl groups as defined in claim 6, haloalkyl groups as defined in claim 6, alkoxyalkyl groups as defined in claim 6, aryl groups as defined in claim 11, aryloxy groups as defined in claim 6 and aralkyl groups as defined in claim 11;

said heteroaryl groups are 5- to 7-membered aromatic heterocyclic groups containing from 1 to 3 heteroatoms selected from the group consisting of sulfur atoms, oxygen atoms and nitrogen atoms, said groups optionally being substituted with at least one substituent selected from the group consisting of nitro groups, cyano groups, amino groups, alkyl groups as defined in claim 6, haloalkyl groups as defined in claim 6, alkoxyalkyl groups as defined in claim 6, aryloxy groups as defined in claim 6 and alkoxy groups as defined in claim 6.

13.   An optical device according to claim 12, wherein m and n are each 0 and X is a linking unit of formula -A-B-C- wherein A and C each represent a methylene group and B is selected from the group consisting of O, S, SO_2, NR^3, $N^+(R^{3'})(R^{3''})$ and $C(R^4)(R^5)$ wherein R^3, $R^{3'}$, $R^{3''}$, R^4, R^5 and R^6 are as defined in claim 12.

14.   An optical device according to claim 12, wherein m and n are each 0 and X is a linking unit of formula -A-B-C- wherein A and C each represent a methylene group and B is selected from the group consisting of O, S, SO_2, NR^3 wherein R^3 is selected from the group consisting of hydrogen atoms and alkyl groups having from 1 to 6 carbon atoms which are optionally substituted with a group of formula $-N^+(R^7)_3$ wherein each group R^7 is the same or different and is selected from the group consisting of hydrogen atoms and alkyl groups having from 1 to 6 carbon atoms, $N^+(R^{3'})(R^{3''})$ wherein $R^{3'}$ and $R^{3''}$ are the same or different and each represents an alkyl group having from 1 to 6 carbon atoms which is optionally substituted with a group of formula $-N^+(R^7)_3$ wherein each group R^7 is the same or different and is selected from the group consisting of hydrogen atoms and alkyl groups having from 1 to 6 carbon atoms, and $C(R^4)(R^5)$ wherein R^4 and R^5 are the same or different and each is selected from the group consisting of hydrogen atoms, alkyl groups having from 1 to 10 carbon atoms, alkoxy groups having from 1 to 10 carbon atoms and alkyl groups having from 1 to 10 carbon atoms which are substituted with a substituent selected from the group consisting of aryl groups, heteroaryl groups, fluorenyl groups and spirobifluorenyl groups, said aryl, heteroaryl, fluorenyl and spirobifluorenyl groups being substituted with a disubstituted amino group the substituents of which are the same or different and are selected from the group consisting of aryl groups, heteroaryl groups, fluorenyl groups and spirobifluorenyl groups.

15.   An optical device according to claim 12, wherein m and n are each 0 and X is a linking unit of formula -A-B-C- wherein A and C each represent a methylene group and B is selected from the group consisting of O, S, SO_2, $N^+(R^{3'})(R^{3''})$ wherein $R^{3'}$ and $R^{3''}$ are the same or different and each represents an alkyl group having from 1 to 3 carbon atoms which is optionally substituted with a group of formula $-N^+(R^7)_3$ wherein each group R^7 is the same or different and is an alkyl group having from 1 to 3 carbon atoms, and

$C(R^4)(R^5)$ wherein R^4 and R^5 are the same or different and each is selected from the group consisting of hydrogen atoms, alkyl groups having from 1 to 3 carbon atoms and alkoxy groups having from 5 to 10 carbon atoms.

16.   An optical device according to claim 12, wherein m and n are each 0 and X is a linking unit of formula -A-B-C- wherein A and C each represent a methylene group and B is a group of formula $C(R^4)(R^5)$ wherein each of R^4 and R^5 is a hydrogen atom or R^4 represents a hydrogen atom and R^5 represents an alkoxy group having from 7 to 10 carbon atoms.

17.   An optical device according to claim 12, wherein m and n are each 0 and X is a linking unit of formula -A-B-C- wherein A and C each represent O or S and B is selected from the group consisting of O, S, SO_2, NR^3, $N^+(R^{3'})(R^{3''})$ and $C(R^4)(R^5)$ wherein R^3, $R^{3'}$, $R^{3''}$, R^4, R^5 and R^6 are as defined in claim 12.

18.   An optical device according to claim 12, wherein m and n are each 0 and X is a linking unit of formula -A-B-C- wherein A and C each represent O or S and B is a group of formula $C(R^4)(R^5)$ wherein R^4 and R^5 are the same or different and each represents a hydrogen atom or an alkyl group having from 1 to 10 carbon atoms.

19.   An optical device according to claim 12, wherein m and n are each 0 and X is a linking unit of formula -A-B-C- wherein A and C each represent O and B is a group of formula $C(R^4)(R^5)$ wherein R^4 and R^5 are the same or different and each represents an alkyl group having from 1 to 3 carbon atoms.

20.   An optical device according to claim 12, wherein the unit of formula (III) is selected from the following group:
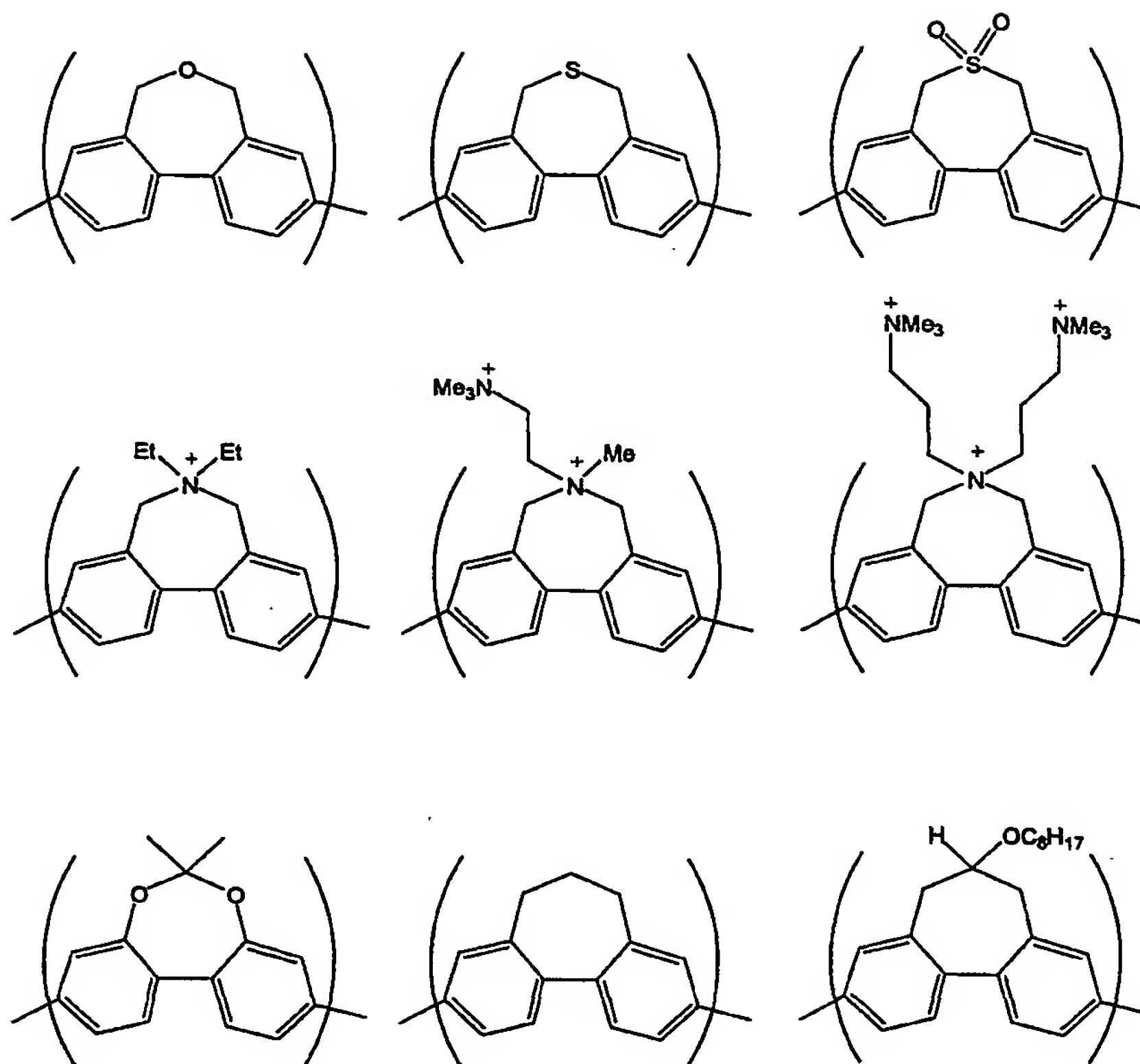
21.   A semiconductive copolymer in which one of the repeat units is a group of formula (II) as defined in any one of claims 8 to 10 or a semiconductive homopolymer in which the repeat unit is a group of formula (II) as defined in any one of claims 8 to 10, with the proviso that, where Y^1 and Y^2 each represent a single bond, X may not represent a linking unit selected from the group consisting of -CO-O-CO-, -CO-NH-CO- and -O-P(O)(OH)-O-, and where Y^1 represents a phenyl group which is fused with the phenyl group to which it is attached to form a naphthalenyl group and Y^2 represents a phenyl group which is fused with the phenyl group to which it is attached to form a naphthalenyl group, X may not represent a group of formula -O-CH$_2$-O-.

22.   A semiconductive copolymer in which one of the repeat units is a group of formula (III) as defined in any one of claims 11 to 20 or a semiconductive homopolymer in which the repeat unit is a group of formula (III) as defined in any one of claims 11 to

20, with the proviso that, where Y^1 and Y^2 each represent a single bond, X may not represent a linking unit selected from the group consisting of -CO-O-CO-, -CO-NH-CO- and -O-P(O)(OH)-O-.

23.   A semiconductive copolymer according to claim 21 or claim 22 selected from the group consisting of alternating AB copolymers and terpolymers, and statistical copolymers and terpolymers.

24.   A semiconductive copolymer according to claim 23 selected from copolymers of the following general formulae (IV), (V), (VI) and (VII):
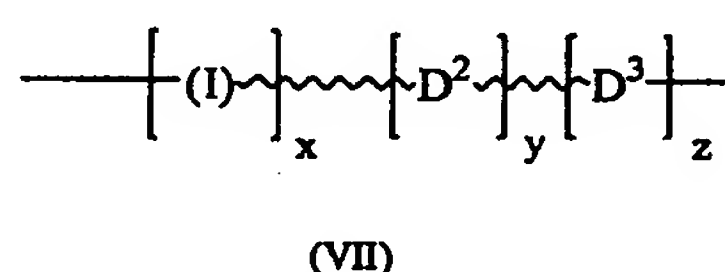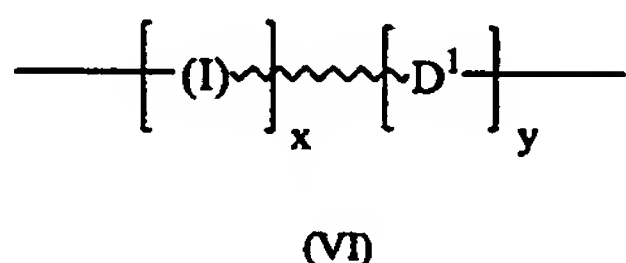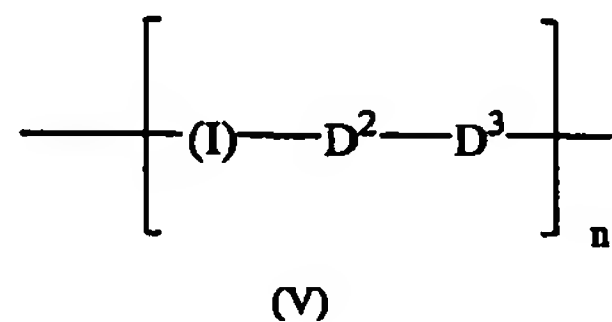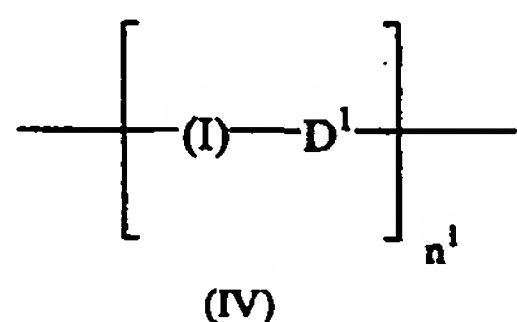
(IV)

(V)

(VI)

(VII)

wherein:

(I) is a repeat unit as defined above, D^1, D^2 and D^3 are repeat units which are conjugated with the adjacent units in the polymer chain, n^1 is an integer greater than 3, the ratio of x:y is from 99:1 to 1:99, and the ratio of x:(y+z) is from 99:1 to 1:99.

25.   A semiconductive copolymer according to claim 24, wherein the ratio x:y is from 10:90 to 50:50 and the ratio x:(y+z) is from 90:10 to 50:50.

26.   A semiconductive copolymer according to claim 24, wherein the ratio x:y is from 10:90 to 45:55 and the ratio x:(y+z) is from 90:10 to 45:55.

27. A semicondutive copolymer according to any one of claims 24 to 26, wherein the repeat units D^1, D^2 and D^3 are selected from the following conjugated units of formulae (VIII), (IX), (X), (XI), (XII), (XIII), (XIV) and (XV):
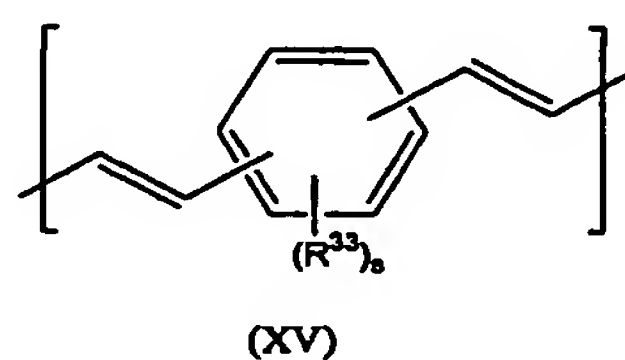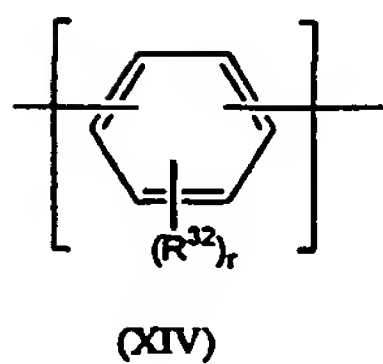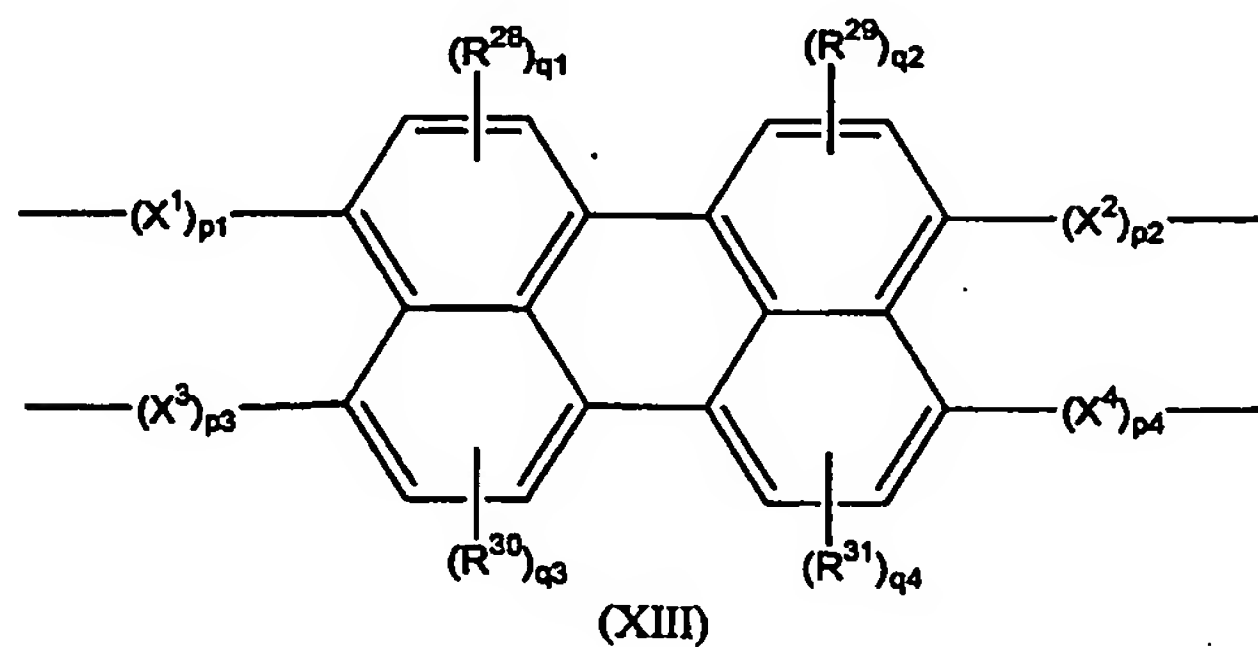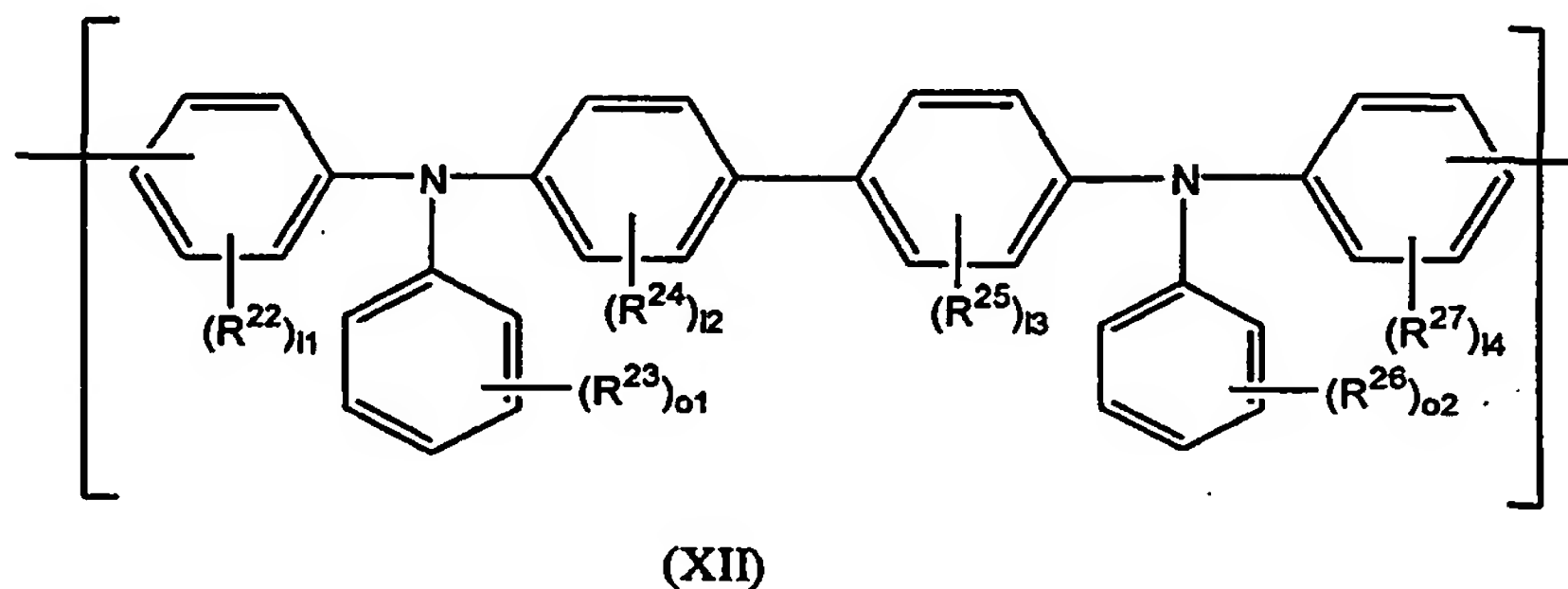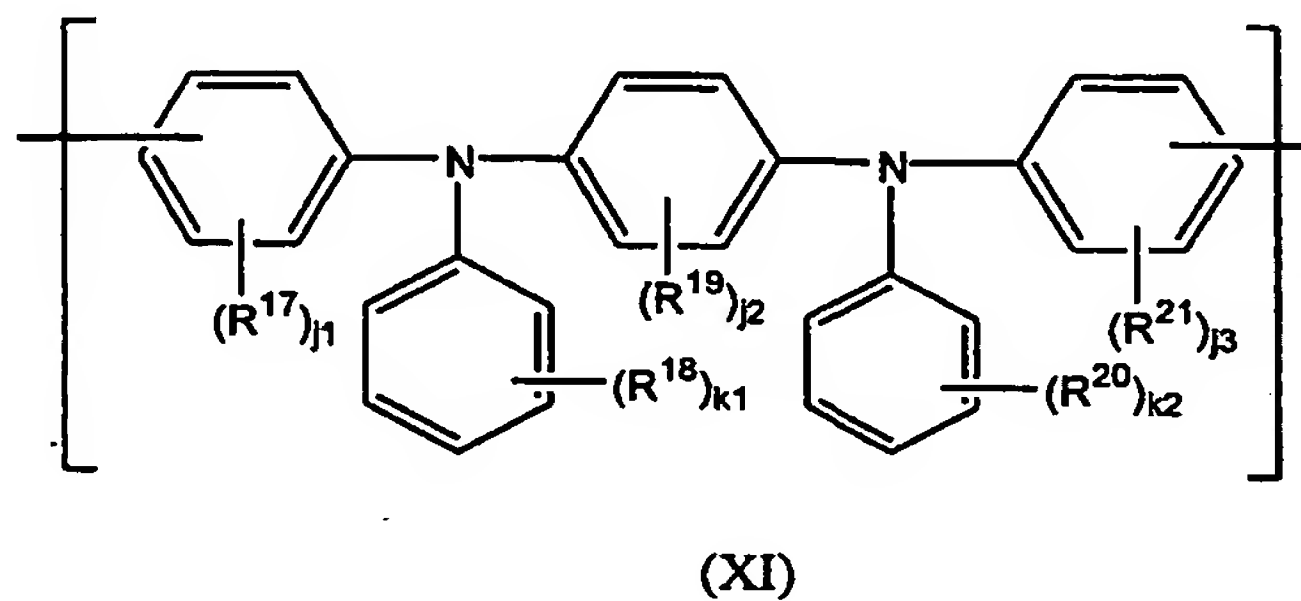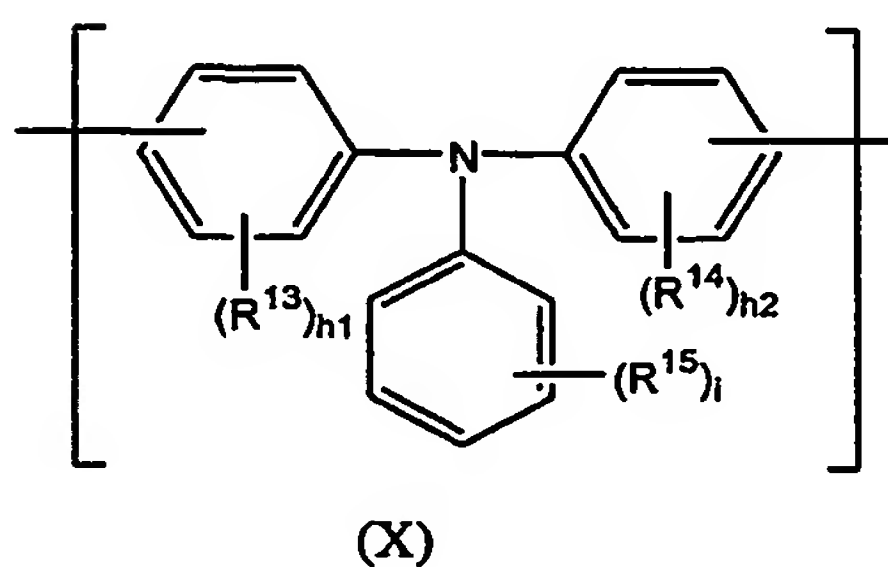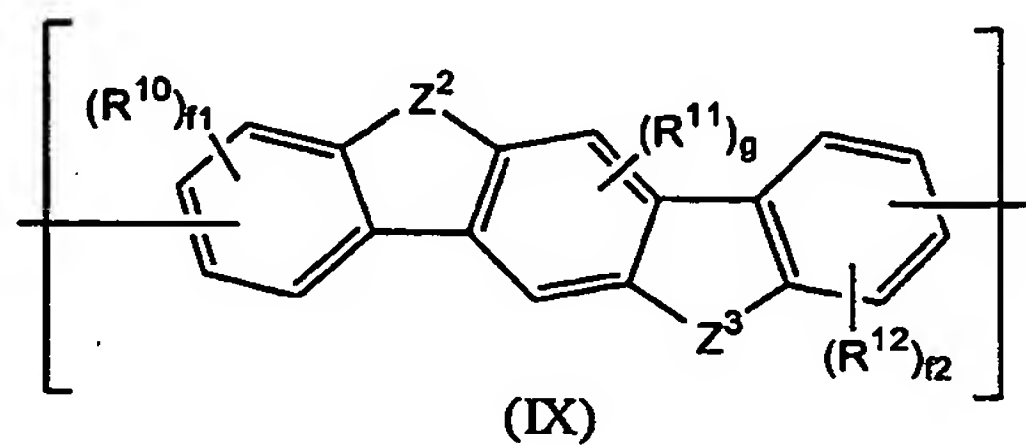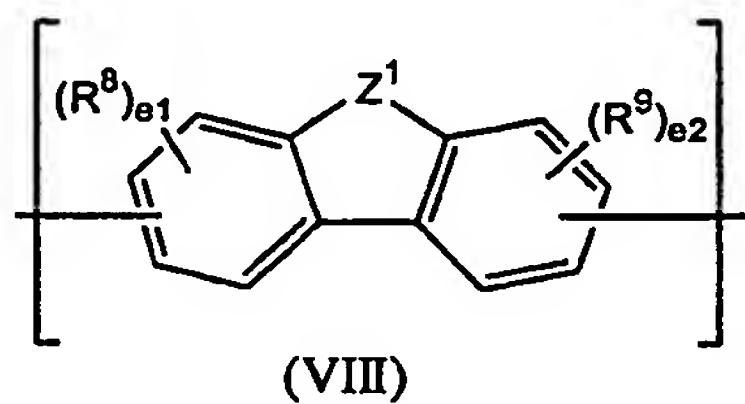
(VIII)

(IX)

(X)

(XI)

(XII)

(XIII)

(XIV)

(XV)

wherein:

each of R^8 to R^{15} and R^{17} to R^{33} is the same or different and is selected from the group consisting of alkyl groups as defined in claim 6, haloalkyl groups as defined in claim 6, alkoxy groups as defined in claim 6, alkoxyalkyl groups as defined in claim 6, aryl groups as defined in claim 11, aryloxy groups as defined in claim 6, aralkyl groups as defined in claim 11 and groups of formula $-COR^{16}$ wherein R^{16} is selected from the group consisting of hydroxy groups, alkyl groups as defined in claim 6, haloalkyl groups as defined in claim 6, alkoxy groups as defined in claim 6, alkoxyalkyl groups as defined in claim 6, aryl groups as defined in claim 11, aryloxy groups as defined in claim 6, aralkyl groups as defined in claim 11, amino groups, alkylamino groups the alkyl moiety of which is as defined in claim 6, dialkylamino groups wherein each alkyl moiety is the same or different and is as defined in claim 6, aralkyloxy groups the aralkyl moiety of which is as defined in claim 11 and haloalkoxy groups comprising an alkoxy group as defined in claim 6 which is substituted with at least one halogen atom;

each of Z^1, Z^2 and Z^3 is the same or different and is selected from the group consisting of O, S, SO, SO_2, NR^3, $N^+(R^{3'})(R^{3''})$, $C(R^4)(R^5)$, $Si(R^{4'})(R^{5'})$ and $P(O)(OR^6)$, wherein R^3, $R^{3'}$, $R^{3''}$, R^4, R^5, $R^{4'}$, $R^{5'}$ and R^6 are as defined in claim 12;

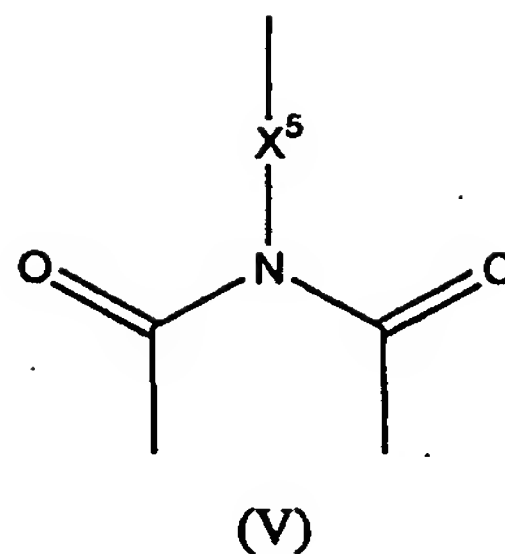each of X^1, X^2, X^3 and X^4 is the same or different and is selected from:

   aryl moietys as defined in claim 6;

   straight or branched-chain alkylene groups having from 1 to 6 carbon atoms;

   straight or branched-chain alkenylene groups having from 2 to 6 carbon atoms; and

   straight or branched-chain alkynylene groups having from 1 to 6 carbon atoms; or

   X^1 and X^2 together and/or X^3 and X^4 together can represent a linking group of formula (V) below:

$$\mathbf{(V)}$$

wherein X^5 represents an aryl moiety as defined in claim 6;

each of e1, e2, f1 and f2 is the same or different and is 0 or an integer of 1 to 3;

each of g, q1, q2, q3 and q4 is the same or different and is 0, 1 or 2;

each of h1, h2, j1, j2, j3, l1, l2, l3, l4, r and s is the same or different and is 0 or an integer of 1 to 4;

each of i, k1, k2, o1 and o2 is the same or different and is 0 or an integer of 1 to 5; and

each of p1, p2, p3 and p4 is 0 or 1.

28.   A semiconductive copolymer according to claim 27, wherein the repeat unit (I) is a repeat unit of formula (II) as defined in any one of claims 8 to 10.

29.   A semiconductive copolymer according to claim 27, wherein the repeat unit (I) is a repeat unit of formula (III) as defined in any one of claims 11 to 20.

30.   A semiconductive copolymer according to any one of claims 27 to 29, wherein the repeat units D^1, D^2 and D^3 are selected from the group consisting of units of formulae (VIII), (IX), (XIV) and (XV) as defined in claim 27.

31.   A semiconductive copolymer according to any one of claims 27 to 29, wherein the repeat unit D^1, D^2 or D^3 is a unit of formula (VIII) wherein Z^1, Z^2 and Z^3 are selected from the group consisting of O, S and $C(R^4)(R^5)$ wherein R^4 and R^5 are as defined in claim 12.

32.   A semiconductive copolymer according to any one of claims 27 to 29, wherein the repeat unit D^1, D^2 or D^3 is a unit of formula (VIII) wherein each of e1 and e2 is 0 and Z^1, Z^2 or Z^3 is a group of formula $C(R^4)(R^5)$ wherein R^4 and R^5 are the same or different and are selected from the group consisting of hydrogen atoms, alkyl groups having from 1 to 10 carbon atoms and alkyl groups having from 1 to 10 carbon atoms which are substituted with a substituent selected from the group consisting of aryl groups as defined in claim 11, heteroaryl groups as defined in claim 12, fluorenyl groups and spirobifluorenyl groups, said aryl, heteroaryl, fluorenyl and spirobifluorenyl groups being substituted with a disubstituted amino group the substituents of which are the same or different and are selected from the group consisting of aryl groups as defined in claim 11, heteroaryl groups as defined in claim 12, fluorenyl groups and spirobifluorenyl groups.

33.   A semiconductive copolymer according to any one of claims 27 to 29, wherein the repeat unit D^1, D^2 or D^3 is a unit of formula (XV) having the following formula:
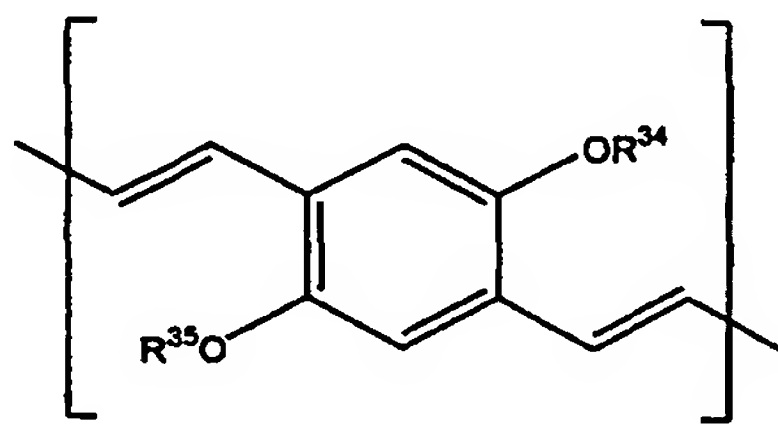

wherein R^{34} and R^{35} are the same or different and each is an alkyl group as defined in claim 6.

34.   A semiconductive copolymer according to claim 24, wherein said copolymer is statistical copolymer of formula (VI) wherein D^1 is as defined in any one of claims 27 and 30 to 32 and the ratio x:y is from 10:90 to 50:50.

35.   A semiconductive copolymer according to claim 24, wherein said copolymer is statistical copolymer of formula (VI) wherein D^1 is as defined in any one of claims 27 and 30 to 32 and the ratio x:y is from 10:90 to 45:55.

36.   A semiconductive copolymer according to claim 24, wherein the repeat unit (I) is as defined in claim 28 and the repeat units D^1, D^2 and D^3 are as defined in claim 30.

37.   A semiconductive copolymer according to claim 24, wherein the repeat unit (I) is as defined in claim 29 and the repeat units D^1, D^2 and D^3 are as defined in claims 31 or 33.

38.   A semiconductive copolymer according to claim 24, wherein the repeat unit (I) is as defined in claim 29 and the repeat units D^1, D^2 and D^3 are as defined in claim 32 or claim 33.

39.   A semiconductive copolymer according to claim 24, wherein said copolymer is a stastistical copolymer of formula (VI) wherein the repeat unit (I) is as defined in claim 29, the repeat units D^1, D^2 and D^3 are as defined in claims 32 or 33 and and the ratio x:y is from 10:90 to 50:50.

40.   A semiconductive copolymer according to claim 24, wherein said copolymer is a stastistical copolymer of formula (VI) wherein the repeat unit (I) is as defined in claim 29, the repeat units D^1, D^2 and D^3 are as defined in claims 32 or 33 and and the ratio x:y is from 10:90 to 45:55.

41.   An optical device comprising a substrate and at least one semiconductive polymer supported by said substrate, wherein said semiconductive polymer is a semiconductive copolymer according to any one of claims 23 to 40.

42.   A monomer selected from monomers of formulae Y^3-E-Y^4 and W^1-E-W^2, wherein:

E is a repeat unit of formula (I), (II) or (III) as defined in any one of claims 1 to 20;

D is a repeat unit of formula D^1, D^2 or D^3 as defined in any one of claims 24, 27 and 31 to 33;

Y^3 and Y^4 are leaving groups;

W^1 and W^2 are selected from the group consisting of boronic acid groups [$B(OH)_2$], boronate ester groups of formula $B(OR^{35})_2$ wherein R^{35} is selected from the group consisting of alkyl groups as defined in claim 6 and aryl groups as defined in claim 11 or the two R^{35} groups together represent a straight or branched chain alkylene group having from 2 to 10 carbon atoms, and boranes of formula $B(OR^{36})_2$ wherein R^{36} is selected from the group consisting of alkyl groups as defined in claim 6, aryl groups as defined in claim 11 and aralkyl groups as defined in claim 11; and

n^1 is an integer greater than 3.

43.   A monomer according to claim 42, wherein the leaving groups Y^3 and Y^4 are bromine or iodine.

44.   A monomer according to claim 42, wherein the substituents W^1 and W^2 are boronate ester groups of formula $B(OR^{35})_2$ wherein the two groups R^{35} together represent an alkylene group having from 2 to 6 carbon atoms.
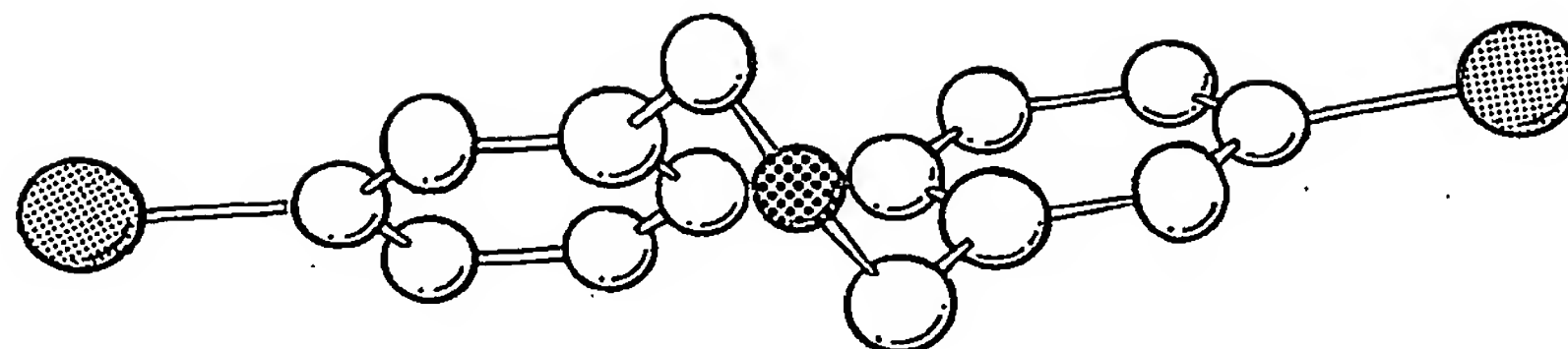

45.   A process for the preparation of a random statistical conjugated polymer comprising reacting, in the presence of a palladium (0) or palladium (II) catalyst and a base, x^1 moles of a monomer of formula Y^5-F^1-Y^6, y^1 moles of W^3-F^1-W^4 and z^1 moles of a monomer of formula W^5-G^1-W^6, wherein

Y^5 and Y^6 are leaving groups,

W^3, W^4, W^5 and W^6 are selected from the group consisting of boronic acid groups [$B(OH)_2$], boronate ester groups of formula $B(OR^{35})_2$ and boranes of formula $B(OR^{36})_2$ wherein R^{35} and R^{36} are as defined in claim 42,

F^1 and G^1 are radicals the nature of which is such that, on polymerisation, the groups F^1 and G^1 in the resulting polymerisation product are conjugated, and

the molar ratio $x^1:(y^1+z^1)$ is 1:1,

to give a random statistical conjugated polymer of formula (XVI) below wherein F^1, G^1, x^1, y^1 and z^1 are as defined above, the molar ratio $(x^1+y^1):z^1$ being greater than 1:

$$-\left(F^1\right)_{x^1+y^1}\!\!\!\!\!\!\!\!\text{\textasciitilde\textasciitilde\textasciitilde}\!\!\!\!\!\left(G^1\right)_{z^1}\!-$$
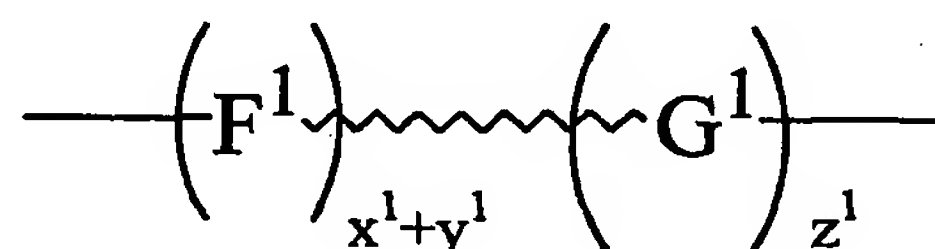
(XVI)

46.   A process according to claim 45, wherein the leaving groups Y^5 and Y^6 are bromine or iodine.

47.   A process according to claim 45 or claim 46, wherein the substituents W^3, W^4, W^5 and W^6 each represent a boronate ester group of formula $B(OR^{35})_2$ wherein the two groups R^{35} in each boronate ester group together represent an alkylene group having from 2 to 6 carbon atoms.

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Fig. 1
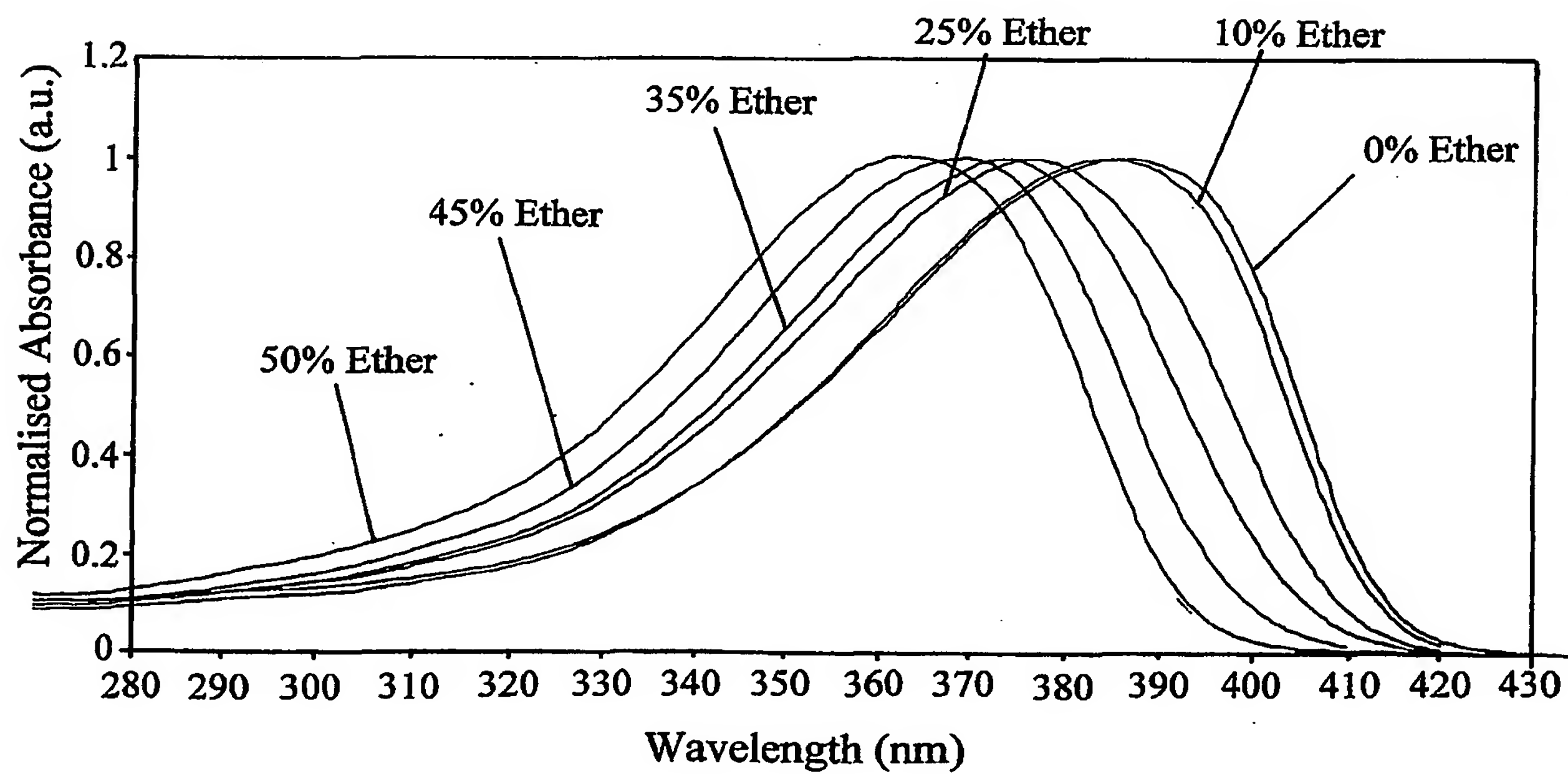
Fig. 2

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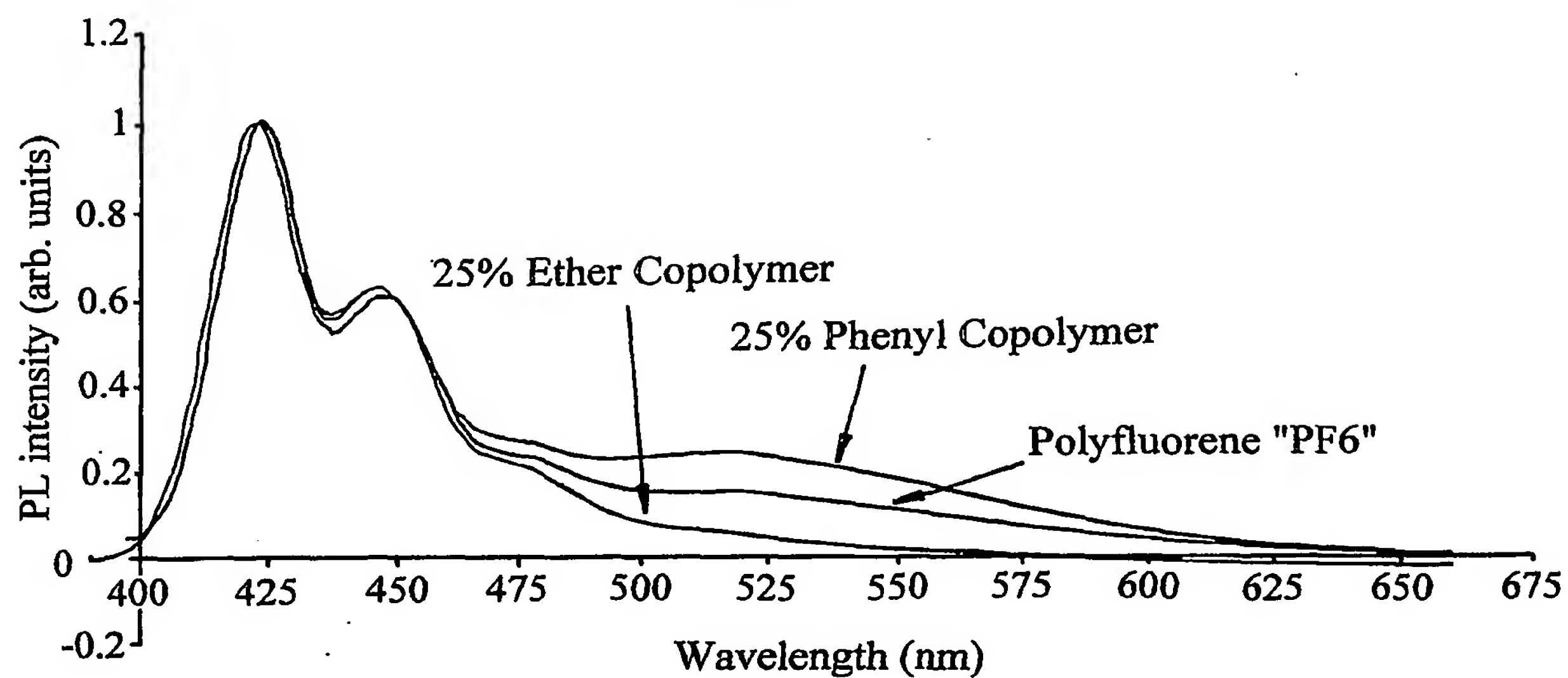
Fig. 3
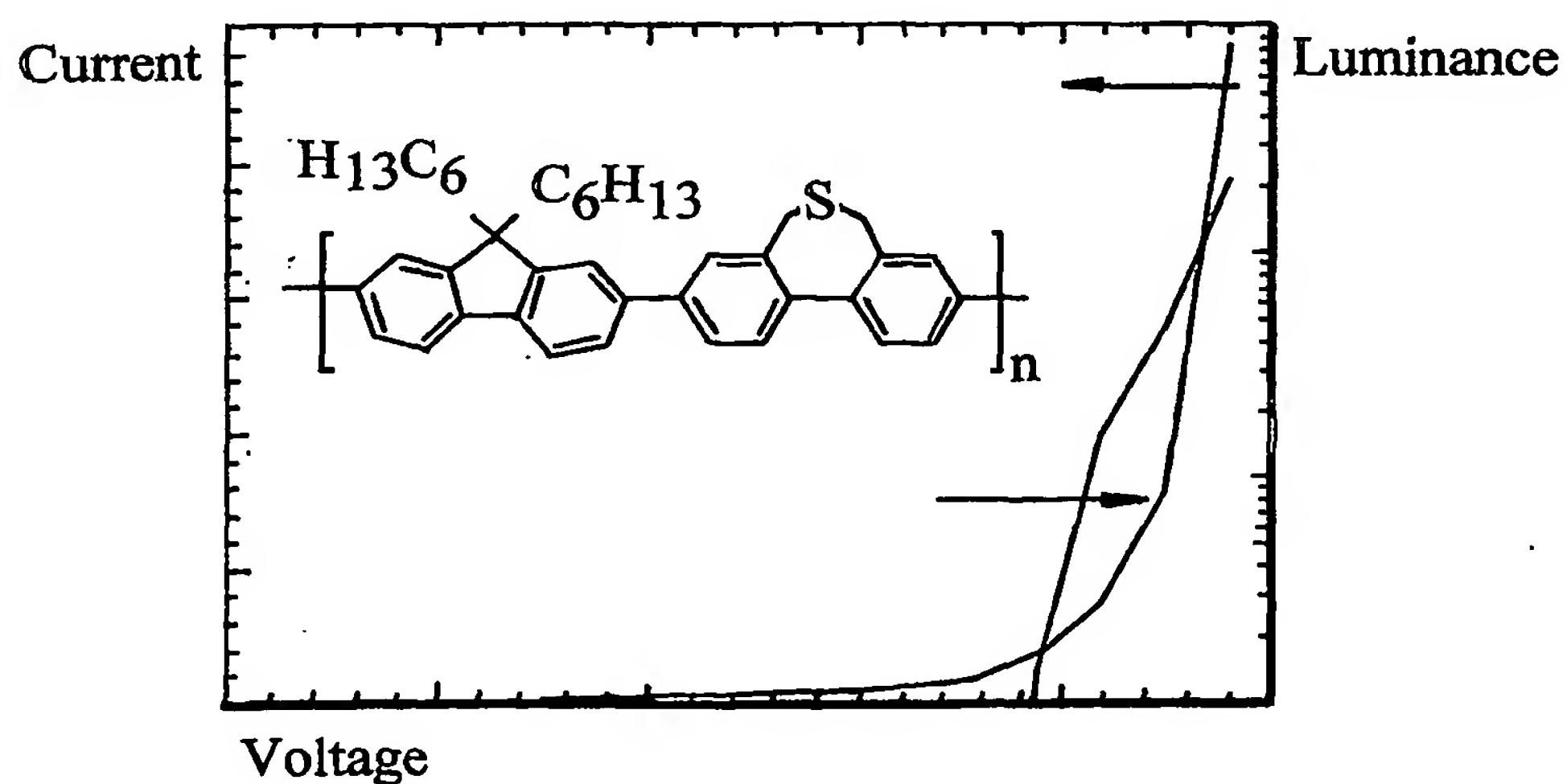
Fig. 4

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Pixel size = 2mm x 3mm
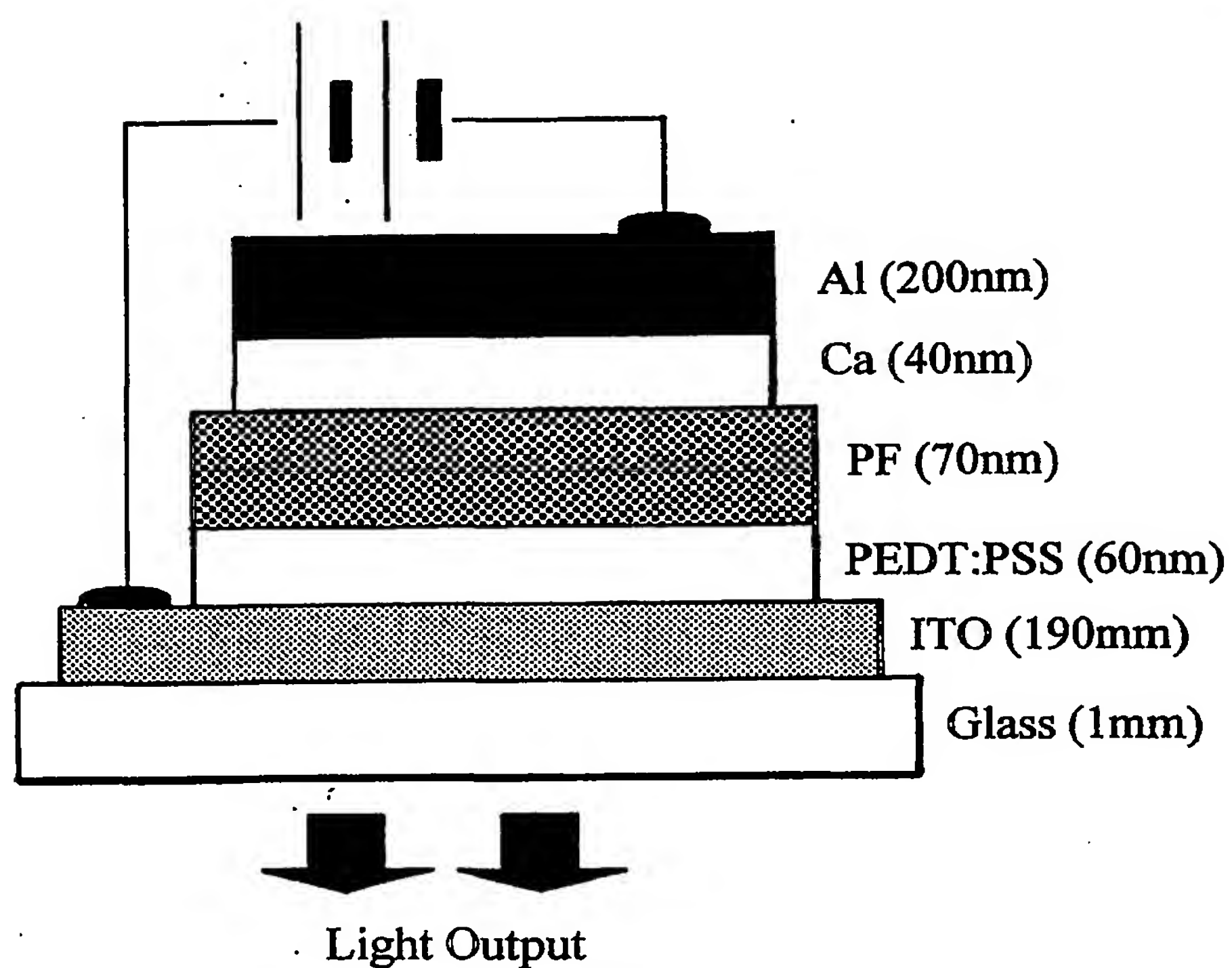

Al (200nm)

Ca (40nm)

PF (70nm)

PEDT:PSS (60nm)

ITO (190mm)
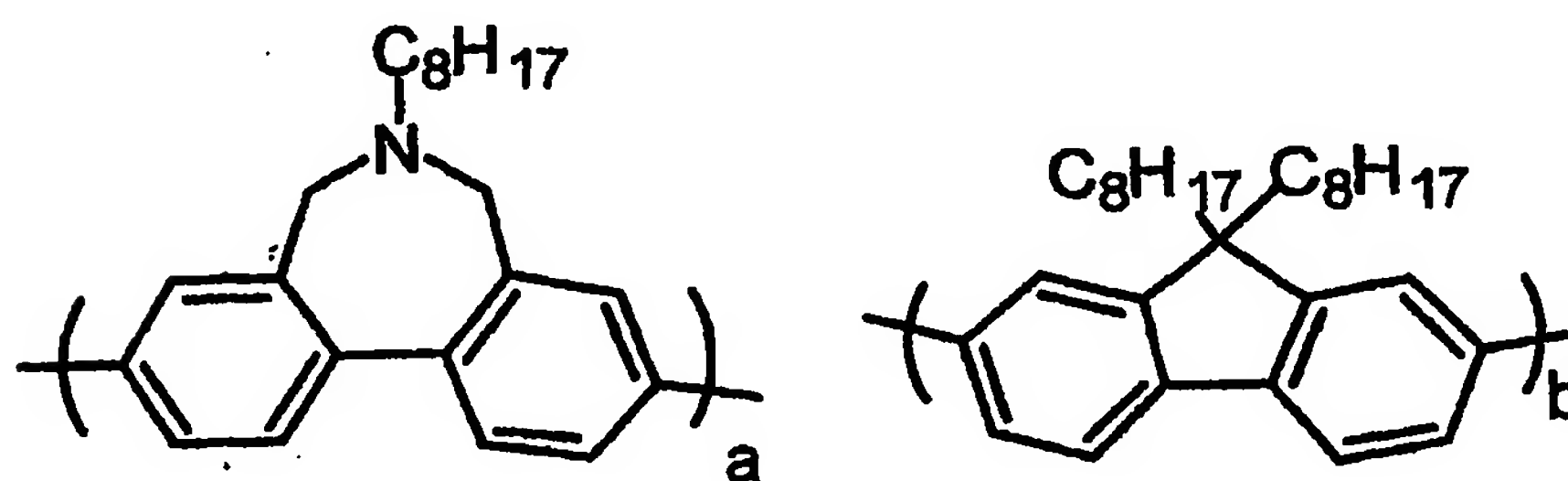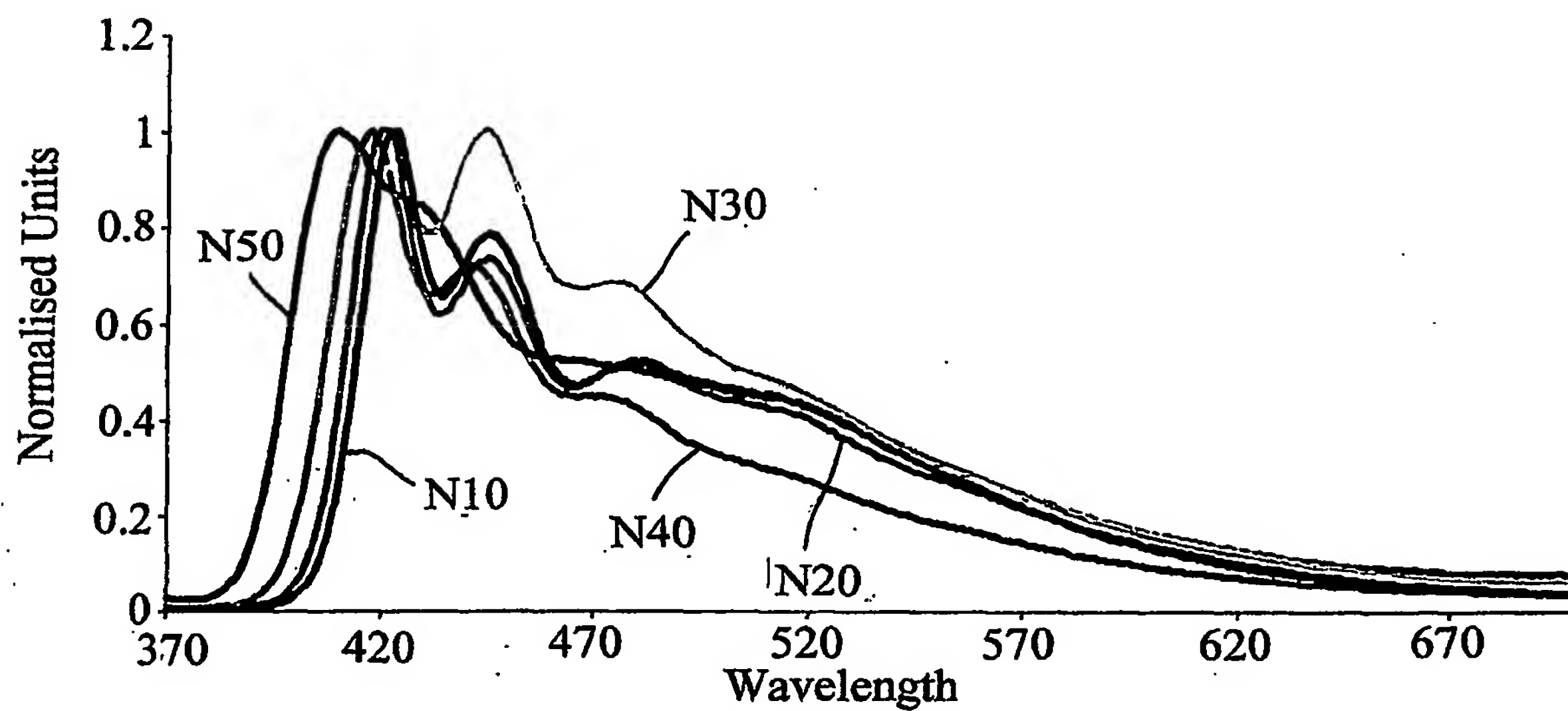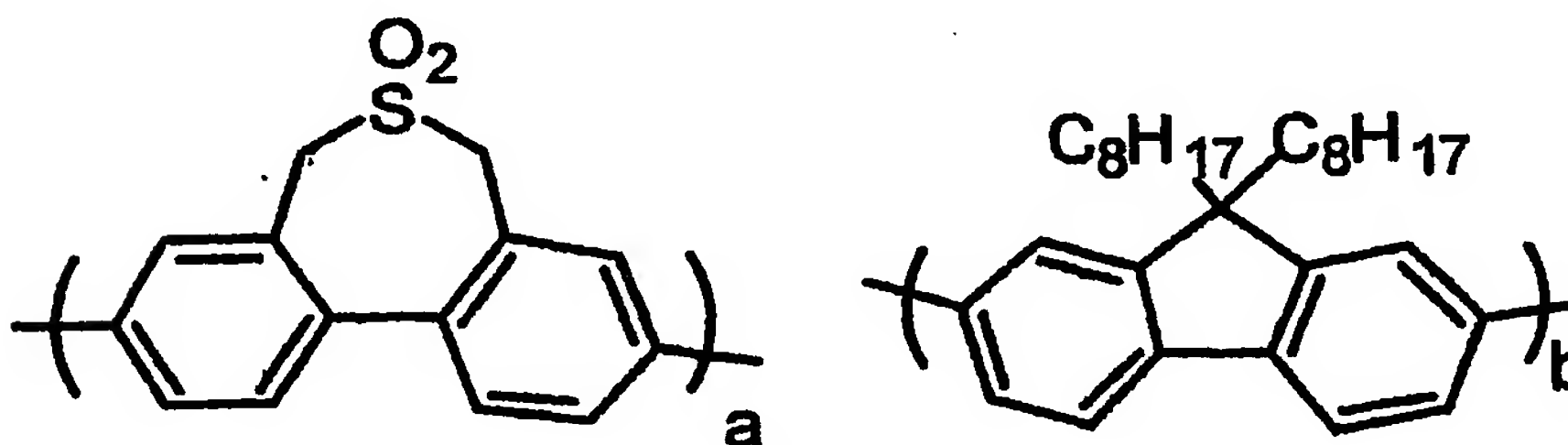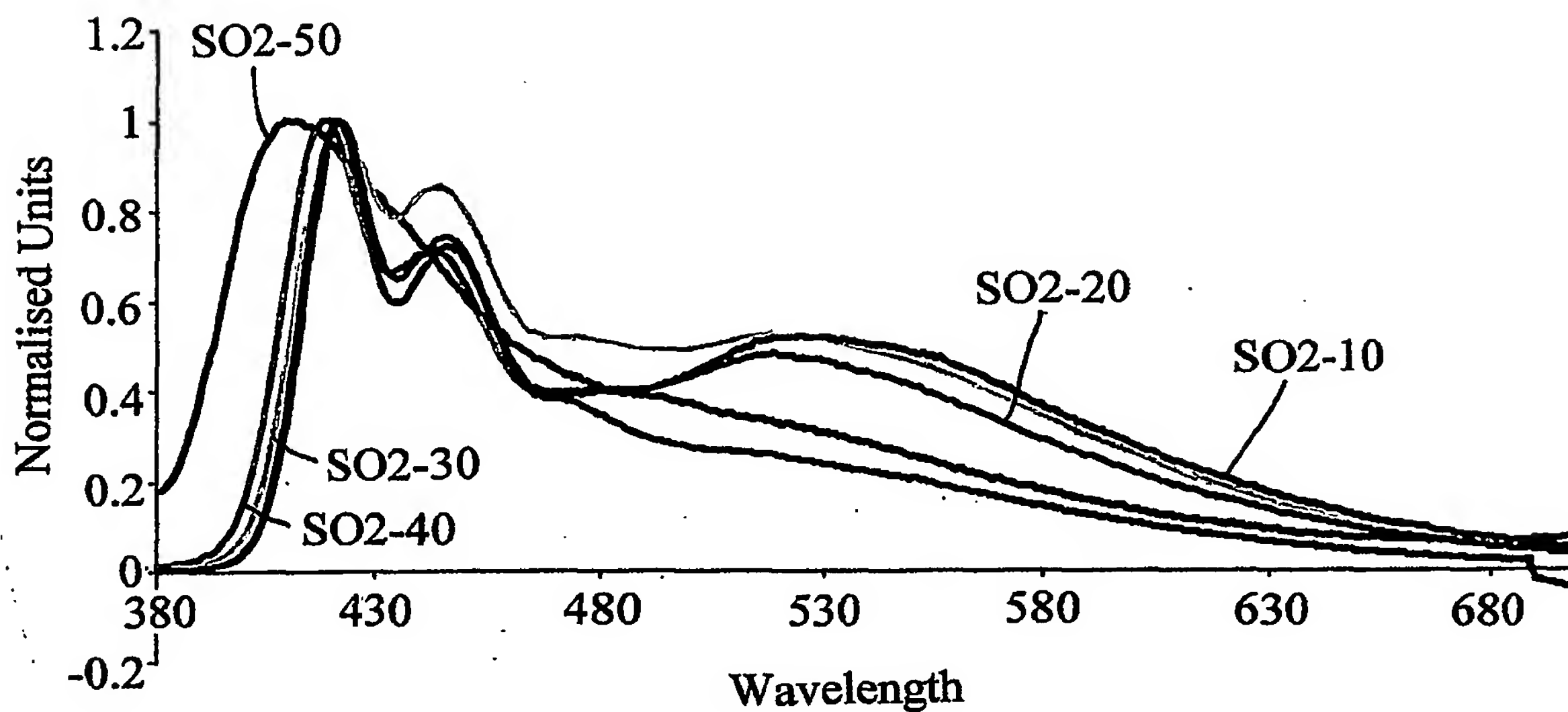
Glass (1mm)

Light Output
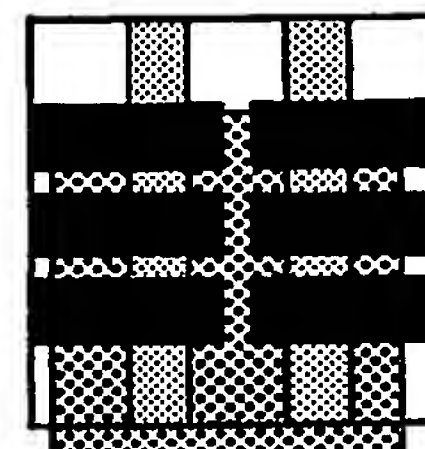
Fig. 5

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Film PL of Octylamine functionalised Twisted Copolymers

N-50 a:b=0.5:0.5
N-40 a:b=0.4:0.6
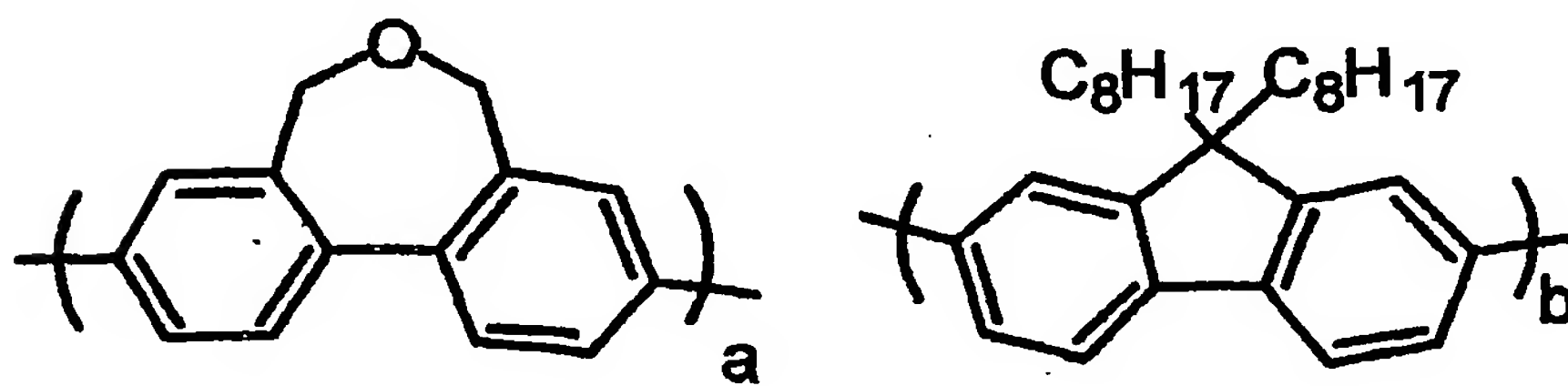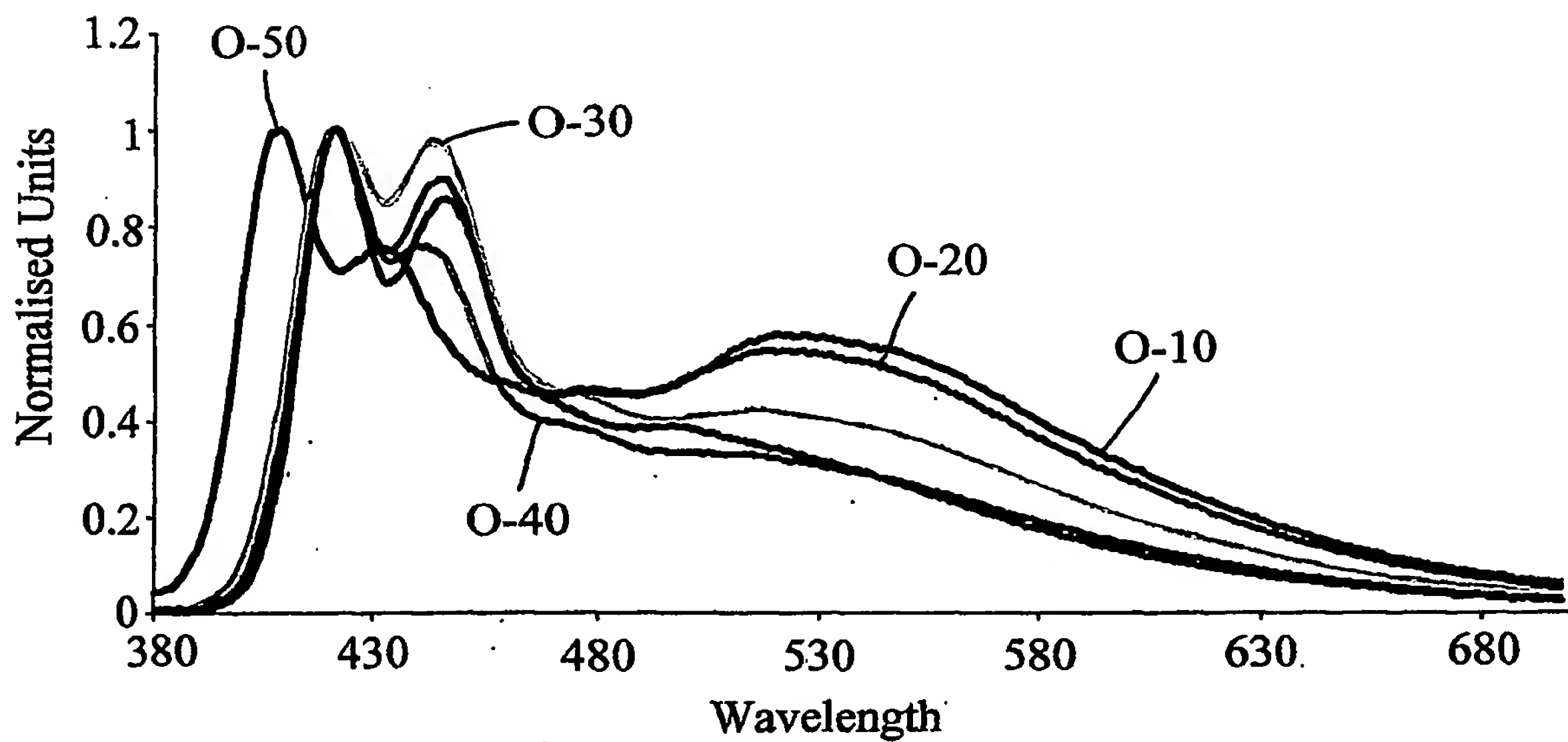N-30 a:b=0.3:0.7
N-20 a:b=0.2:0.8
N-10 a:b=0.1:0.9

Fig. 6

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Film PL of Sulfone Functionalised Twisted Copolymers

SO2-50 a:b=0.5:0.5
SO2-40 a:b=0.4:0.6
SO2-30 a:b=0.3:0.7
SO2-20 a:b=0.2:0.8
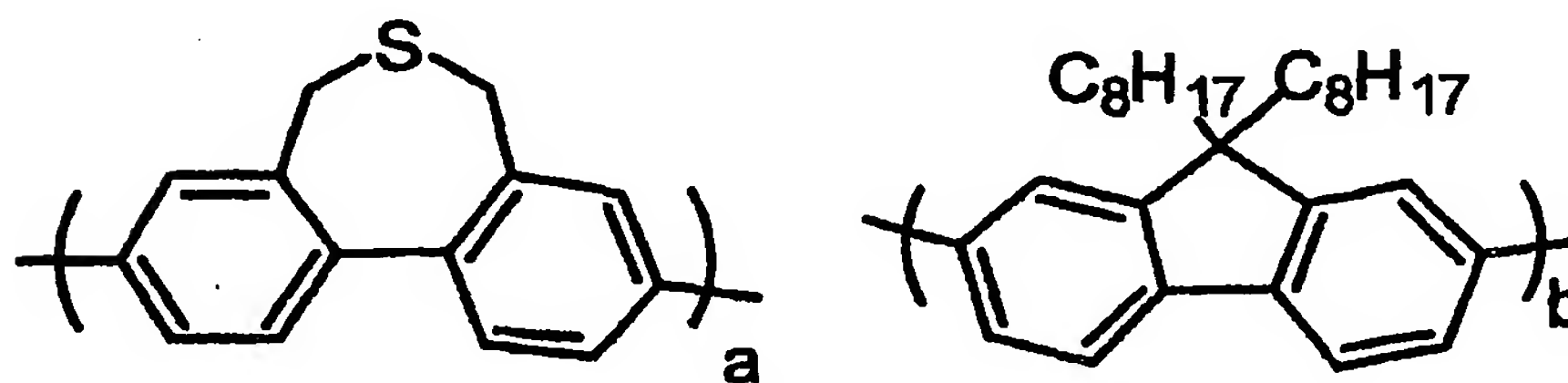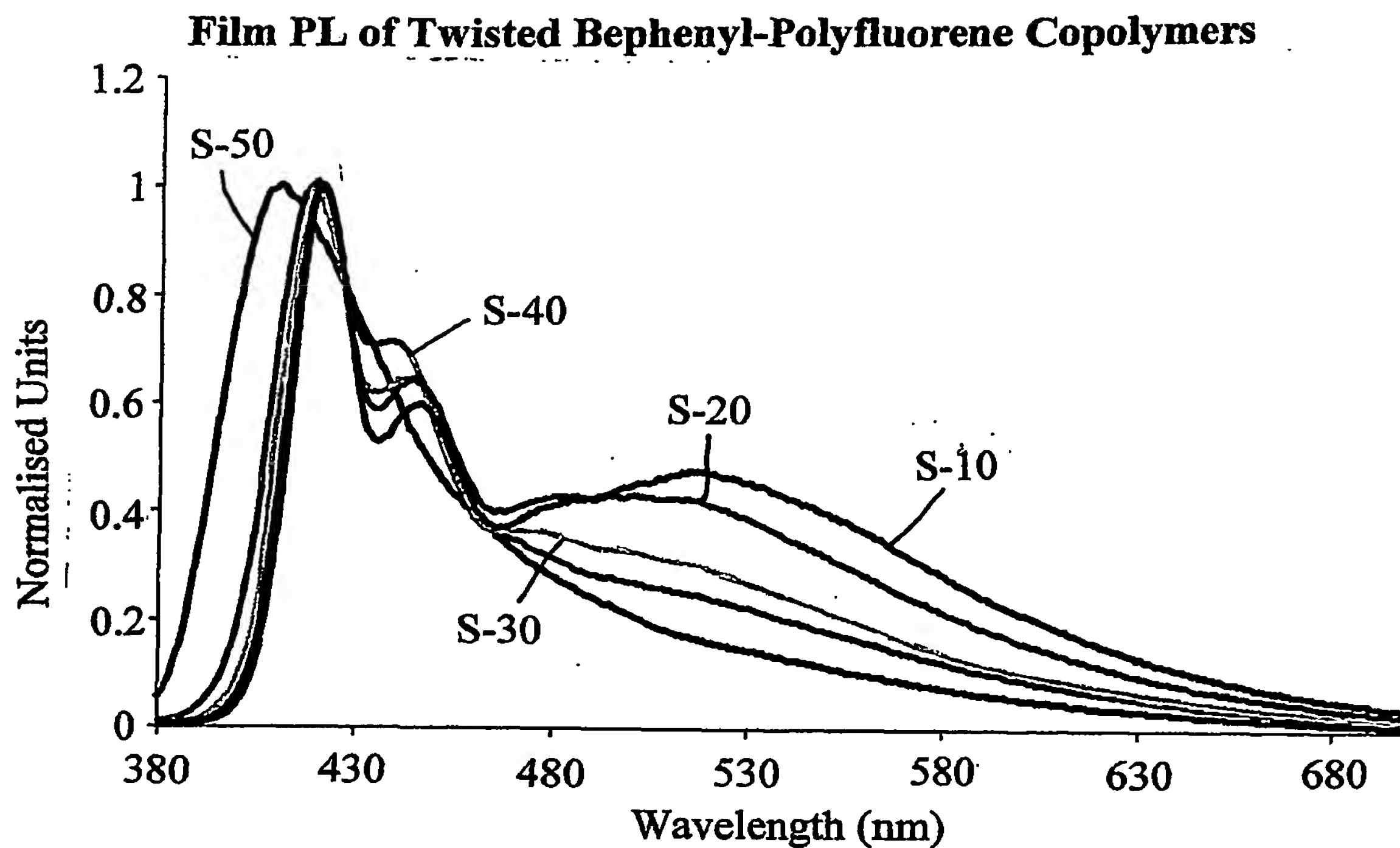SO2-10 a:b=0.1:0.9

Fig. 7

Film PL of Ether functionalised Twisted Copolymers

O-50 a:b=0.5:0.5
O-40 a:b=0.4:0.6
O-30-30 a:b=0.3:0.7
O-20-20 a:b=0.2:0.8
O-10-10 a:b=0.1:0.9

Fig. 8

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Film PL of Twisted Bephenyl-Polyfluorene Copolymers

S-50 a:b=0.5:0.5
S-40 a:b=0.4:0.6
S-30-30 a:b=0.3:0.7
S-20-20 a:b=0.2:0.8
S-10-10 a:b=0.1:0.9

Fig. 9
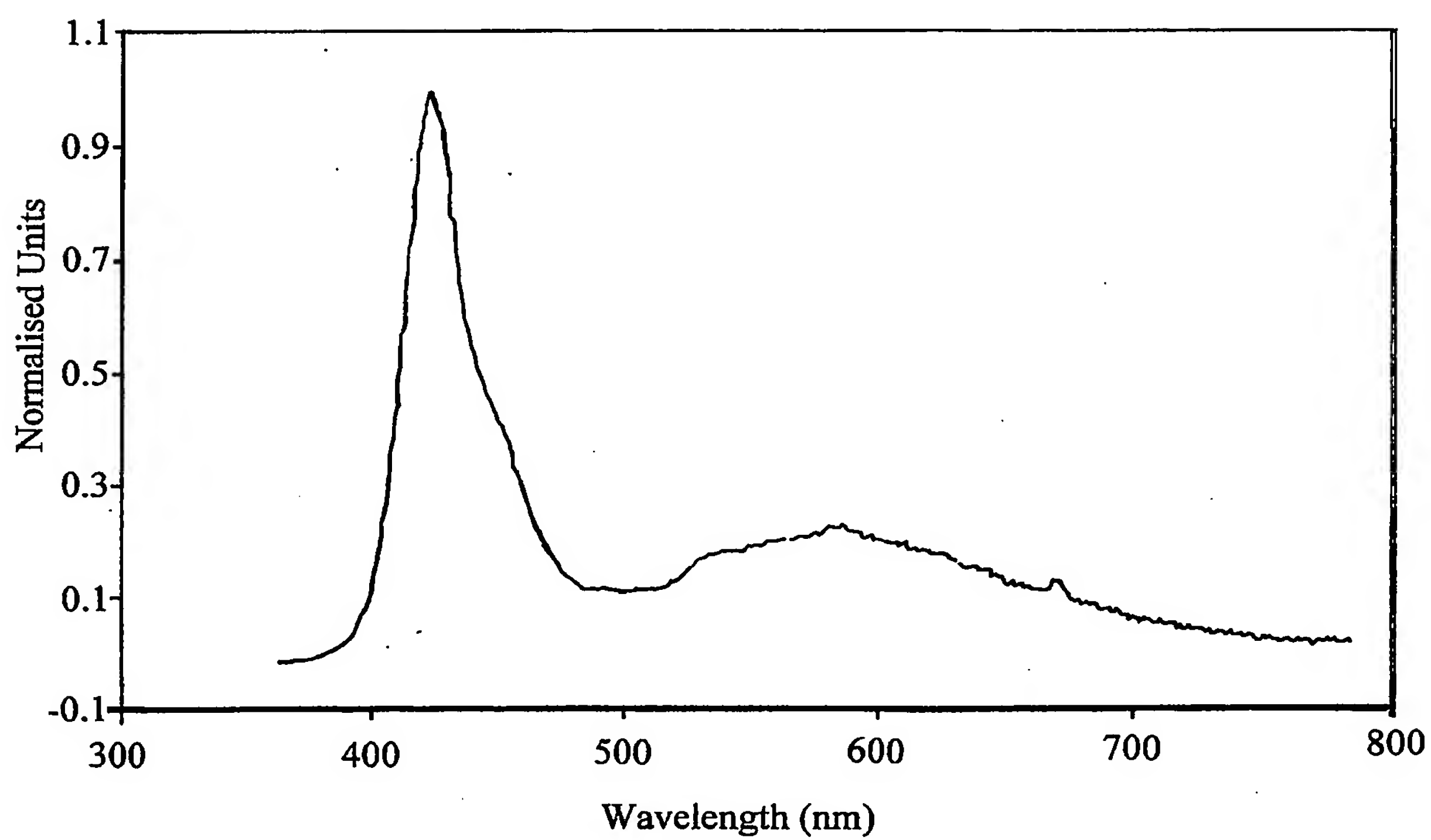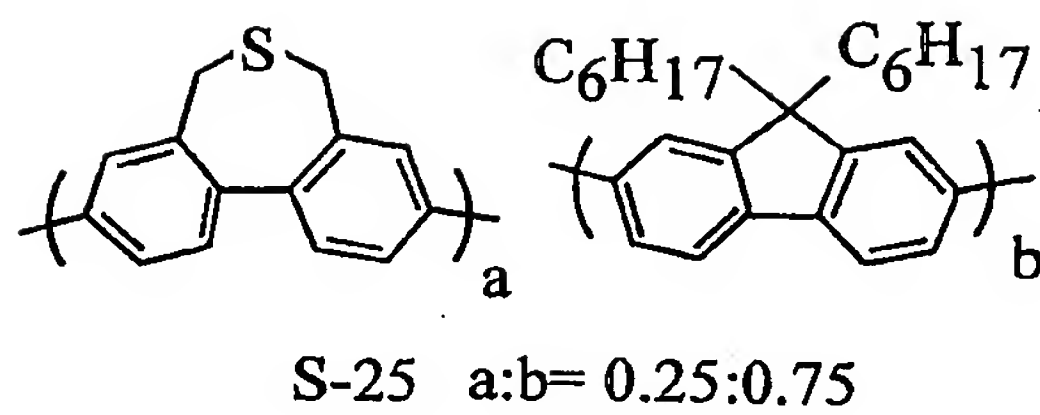
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S-25   a:b= 0.25:0.75

Fig. 10

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08G61/00 C08G61/12 C08G61/02 C08G73/02 C09K11/06
       C07C43/192 H01L51/20 H01L51/30 H05B33/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G C09K C07C H01L H05B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 00 22026 A (KREUDER WILLI ;AXIVA GMBH (DE); BECKER HEINRICH (DE); SPREITZER HU) 20 April 2000 (2000-04-20) page 3-14; claims 1-7	1-19, 21-23, 41-47
X	WO 99 54385 A (DOW CHEMICAL CO) 28 October 1999 (1999-10-28) page 9-14; claims 1-16	1-19, 21-47
X	WO 00 55927 A (TOWNS CARL ROBERT ;DELL RICHARD O (GB); CAMBRIDGE DISPLAY TECH (GB) 21 September 2000 (2000-09-21) page 8-12; claims 1-56	1-19, 21-47
X	WO 00 53656 A (TOWNS CARL ROBERT ;DELL RICHARD O (GB); CAMBRIDGE DISPLAY TECH (GB) 14 September 2000 (2000-09-14) page 5-12; claims 1-20	45-47

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the International search	Date of mailing of the International search report
16 November 2001	26/11/2001

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Wengeler, H

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 777 070 A (INBASEKARAN MICHAEL ET AL) 7 July 1998 (1998-07-07) column 2-8; claims 1-23; examples 1,5-7	1-19, 21-47
X	WO 99 54943 A (DOW CHEMICAL CO) 28 October 1999 (1999-10-28) page 2-6; claims 1-4,7-14,17-20; examples 1,4	1-19, 21-47
X,P	WO 01 42331 A (BECKER STEFAN ;MUELLEN KLAUS (DE); MARSITZKY DIRK (DE); SETAYESH S) 14 June 2001 (2001-06-14) page 4-5; claim 1; example 1	1,27

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			WO	0022026 A1	20-04-2000
			EP	1123336 A1	16-08-2001
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			EP	0988337 A1	29-03-2000
			WO	9954385 A1	28-10-1999
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			WO	0053656 A1	14-09-2000
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			EP	1025142 A1	09-08-2000
			TW	412544 B	21-11-2000
			WO	9920675 A1	29-04-1999
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WO 0142331	A	14-06-2001	AU	1540001 A	18-06-2001
			WO	0142331 A1	14-06-2001